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1927. F

LONDON:
GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C. 4.
1927.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

ERRATA.

VOL., 1927.

Page	Line	
551	14	*after* "m. p. 98—100°" *insert* "which become anhydrous when dried in a vacuum over phosphoric oxide and then melt at 143—145° (decomp.)."
551	19*	*for* "m. p. 151°" *read* "m. p. 155—156°."
551	12*	*for* "m. p. 166—167°" *read* "m. p. 171—172°."
551	4*	*after* "oil" *insert* "(which crystallises on long standing and separates from benzene in colourless prisms, m. p. 114—115°, very soluble in water. Found: C, 55·1; H, 5·0. $C_{11}H_{12}O_6$ requires C, 55·0; H, 5·0%)."
552	2	*for* "m. p. 104—105°" *read* "m. p. 117—118°."

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JOURNAL

OF

THE CHEMICAL SOCIETY.

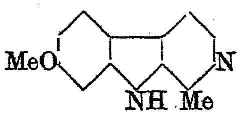
I.—*Harmine and Harmaline. Part IX. A Synthesis of Harmaline.*

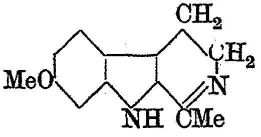
By Richard Helmuth Fred Manske, William Henry Perkin, jun., and Robert Robinson.

In earlier parts of this series of papers several syntheses of derivatives or degradation products of the *harmala* alkaloids have been recorded and the evidence afforded by the syntheses of *apo*harmine (Part VII; Lawson, Perkin, and Robinson, J., 1924, **125**, 626), norharman (Part V; Kermack, Perkin, and Robinson, J., 1921, **119**, 1619), harman (Part IV; Perkin and Robinson, J., 1919, **115**, 968), and *N*-methyltetrahydronorharmine (Part VI; Kermack, Perkin, and Robinson, J., 1922, **121**, 1890) amply suffices to determine the constitution of harmine (I). Some details of the structure proposed for harmaline (II), however, awaited confirmation by a synthetical method and for this reason, in planning the present investigation, although harmine and harmaline are interconvertible, we decided to attempt the synthesis of harmaline in the first place and, furthermore, we hoped to employ a series of reactions such that a successful outcome of the work would have a real bearing on the constitutional problem. After numerous attempts in other directions, only one of which is mentioned in this communication, the synthesis of harmaline has been effected and in such a manner (see below) as strongly to support the adoption of the expression (II) and to exclude (III) as a representation of the constitution of this base. Apart from (II), the synthesis is consistent only with the formula (IV), and we take this opportunity of pointing out that the reactions of harmaline may be satisfactorily interpreted on the hypothesis that (II) and (IV) are tautomerides, the crystallised base being probably (II). It has already been shown (Part VIII; Nishikawa, Perkin, and Robinson, J., 1924, **125**, 657) that methylharmaline and acetylharmaline are

N-substituted derivatives of (IV) and therefore the nucleus exhibits little disinclination to assume this configuration, which probably

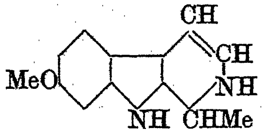
(I.)

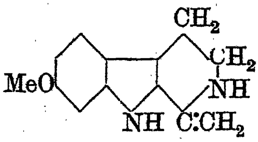




(II.)

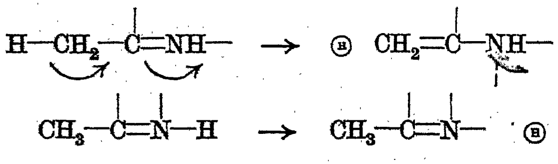
(III.)



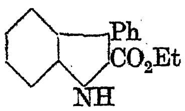


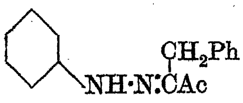
(IV.)

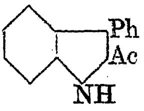
comes into play in the characteristic reactions of harmaline with diazonium salts and with benzaldehyde. On the other hand, the tertiary basic character required by formula (II) is exhibited towards methyl iodide and other alkylating agents and all analogies (compare, for example, the salt formation of ethyl β-aminocrotonate, 1-benzylidene-*N*-methyltetrahydro*iso*quinoline, *iso*papaverine, methylenedihydroquinolines, and of other anhydronium bases) indicate that the double bond in a salt of harmaline is invariably in the position illustrated in (II). We do not conceive the interchange between (II) and (IV) as a direct one but rather as a process dependent on the presence of hydrogen ions, the decomposition of a kation in two directions being responsible for any equilibrium which may be established. The electronic changes and fission involved are represented in the annexed scheme.



Turning to the detail of the synthetical work, the feasibility of our plan in main outline was clearly indicated when we found in a favourable case that E. Fischer's synthesis of indole derivatives could be applied to the monophenylhydrazone of an α-diketone, a member of a class of substances which are very readily accessible in great variety through the Japp–Klingemann reaction (*Ber.*, 1888, **21**, 549; *Annalen*, 1888, **247**, 218). The advantages of this procedure are manifold; indole derivatives can be prepared which are difficult or impossible to obtain in other ways, but apart from this, the Japp–Klingemann reaction gives excellent yields and the stage of reduction of the diazonium salt to a hydrazine is eliminated. Ethyl α-acetyl-β-phenylpropionate condenses directly with benzenediazonium chloride in alkaline-alcoholic solution with extrusion of the acetyl group, and the product, after hydrolysis and treatment with alcoholic hydrogen chloride, yields *ethyl 3-phenylindole-2-carboxylate* (V). On the other hand, an alkaline solution of sodium α-acetyl-β-phenylpropionate and benzenediazonium chloride affords, with extrusion of the carboxyl group, *α-phenylbutane-βγ-dione β-phenylhydrazone* (VI). Boiling concentrated hydrochloric acid induces indole cyclisation of this substance to *2-acetyl-3-phenylindole* (VIII), which yields 3-phenylindole on fusion with sodium hydroxide.


(V.)


(VI.)


(VII.)

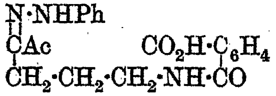
The method was then extended to the preparation of a 2-acetyl-3-β-aminoethylindole derivative and, as appeared in the sequel, we fortunately selected the phthaloyl residue for the protection of the amino-group. Ethyl δ-phthalimido-α-acetylvalerate,

$$C_6H_4(CO)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et$$

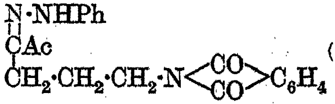
(Gabriel, *Ber.*, 1909, **42**, 1242), was hydrolysed by cold aqueous-alcoholic sodium hydroxide with the formation of the salt

$$CO_2Na{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Na,$$

and this coupled in the alkaline solution with benzenediazonium chloride, losing the carboxyl group and yielding, after acidification, *ζ-o-carboxybenzamidohexane-βγ-dione γ-phenylhydrazone* (VIII). This phthalamic acid was easily converted into the corresponding phthalimide (IX) by means of acetic anhydride.

(VIII.)


$$\begin{array}{ll} \mathrm{N{\cdot}NHPh} & \\ \Vert & \\ \mathrm{CAc} & \mathrm{CO_2H{\cdot}C_6H_4} \\ | & \quad | \\ \multicolumn{2}{l}{\mathrm{CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO}} \end{array}$$

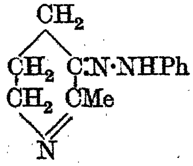

(IX.)

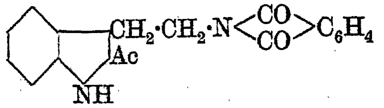
$$\begin{array}{l} \mathrm{N{\cdot}NHPh} \\ \Vert \\ \mathrm{CAc} \\ | \\ \mathrm{CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N{<}{}^{CO}_{CO}{>}C_6H_4} \end{array}$$

At this stage, serious difficulty was encountered in the course of attempts to induce the indole transformation of these phenylhydrazones. The compound (VIII) exhibits a marked tendency to split off phthalic acid with formation of a remarkable tetrahydropicoline derivative (X). This substance is a strong, stable base forming intensely yellow salts and it is best prepared from the phthalamic acid derivative by the action of hydrogen chloride in hot acetic acid solution; further representatives of this series have been similarly obtained and are described in the experimental section. An interesting property of the base is its stability to acids and so far as we are aware it cannot be converted into an indole derivative under the influence of acids or reagents such as zinc chloride. In the light of the theory of the mechanism of the Fischer indole synthesis (Robinson and Robinson, J., 1918, **113**, 639; 1924, **125**, 827), this means that the substance does not occur in the phase containing the group $NHPh{\cdot}NH{\cdot}\overset{|}{C}{=}\overset{|}{C}{-}$, and it is not unreasonable to attribute this circumstance to the plastic, semi-aromatic character of the system $NHPh{\cdot}N{:}C{\cdot}C{:}N{-}$. In such assemblages there is a reduction of unsaturated character and a stability factor which operates against the transfer of the unsaturation to any external group in a tautomeric process.

Further evidence that the hydrazone complex has been modified in character by the associated imino-centre is supplied by the resistance which the base exhibits to hydrolysis. The formation of (X) from (VIII) is doubtless facilitated by, or is even entirely due to, the formation of an intermediate product containing the group $\cdot CMe(OH){\cdot}\overset{|}{N}{\cdot}CO{-}$, and if the nitrogen of the amide group carried no hydrogen atom this preliminary ring closure would, of course, be avoided. Actually it was found possible to obtain the corresponding indole derivative (XI) from (IX) by the use of boiling alcoholic hydrochloric acid, and no other reagent, in our experience, is able to bring about the transformation.

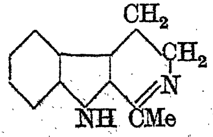
(X.)





(XI.)

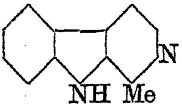
(XII.)

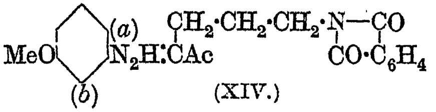


In order to obtain *harmalan*, the name by which we propose to designate *des*methoxyharmaline (since *des*methoxyharmine is termed harman), it was necessary to remove the phthaloyl group from (XI) by hydrolysis, and in this connexion a method was devised which is likely to prove generally serviceable in synthetical investigations involving the use of phthalimide derivatives. The action of hydrazine hydrate in hot alcoholic solution on (XI), followed by treatment of the product with hydrochloric acid, yields, quite smoothly, phthalhydrazide, $C_6H_4(CO)_2(NH)_2$, which is insoluble, and a solution of harmalan hydrochloride. Ing and Manske (compare J., 1926, 2348) have shown that the process is generally applicable as the final stage in Gabriel's synthesis of amines.

Harmalan (XII) crystallises with $10H_2O$ and on oxidation with chromic acid yields harman (aribine, loturine) (XIII).

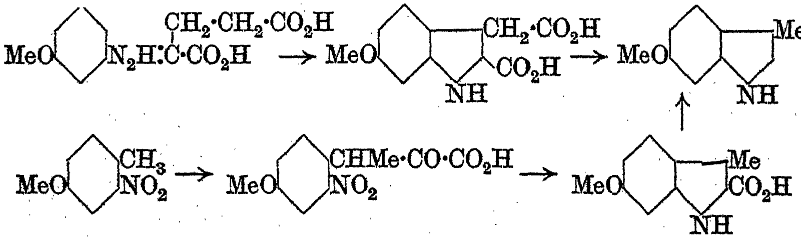
(XIII.)



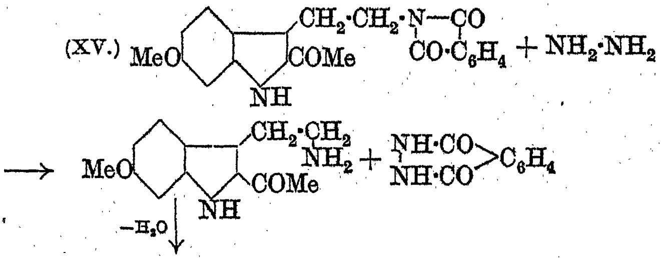


(XIV.)

Replacing benzenediazonium chloride by *m*-methoxybenzenediazonium chloride in the above series of reactions, we obtained a methoxy-derivative of the phthalamic acid (VIII) and then by dehydration the phthalimide derivative (XIV). In this substance, the indole ring might be closed in either of the positions (*a*) and (*b*), but Kermack, Perkin, and Robinson (J., 1921, **119**, 1614) have realised the following scheme, proving not only that closure in position (*a*) is favoured, but also that the reaction involves no alteration in the orientation of the substituents in the benzene ring.



It was found very difficult to transform the hydrazone (XIV) into an indole derivative, but ultimately the change was brought about with the help of *n*-butyl-alcoholic hydrogen chloride. The product (XV) was then converted into harmaline (II) by the hydrazine method as illustrated below.


(XV.)
MeO
$CH_2{\cdot}CH_2{\cdot}N{-}CO$
COMe
$CO{\cdot}C_6H_4$
$+ NH_2{\cdot}NH_2$
NH
MeO
$CH_2{\cdot}CH_2$
NH_2
COMe
NH
$+ \begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}{>}C_6H_4$
$-H_2O$

Harmaline (II.)

The synthetic base was found to be identical with natural harmaline in all respects; the less pure residues were oxidised to harmine, indistinguishable from a specimen derived from *Peganum harmala*.

Although this memoir does not quite complete the account of our investigations in the group of the *harmala* alkaloids, we feel that the present opportunity should be taken in order to pay a tribute of appreciation to the pioneer worker in this field of chemistry. Our researches owe much to the difficult experimental investigations of Otto Fischer which preceded them.

EXPERIMENTAL.

γ-Phthalimidobutyronitrile, $C_6H_4(CO)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$.—In the course of our earlier experiments considerable quantities of this nitrile were prepared with the object of attempting the reduction of the substance to γ-phthalimidobutaldehyde. The latter stage was not accomplished satisfactorily, but the direct replacement of bromine by the cyano-group in γ-bromopropylphthalimide was effected by the use of anhydrous methyl-alcoholic sodium cyanide. This transformation was attempted by Gabriel (*Ber.*, 1889, **22**, 3337) without success and it is certain that the following conditions cannot be greatly varied. Anhydrous hydrogen cyanide (7 c.c.) and sodium iodide (0·5 g.) were added to a solution of sodium methoxide (from 3 g. of sodium) in dry methyl alcohol (50 c.c.); the sodium cyanide was precipitated in a finely-divided condition. After the introduction of γ-bromopropylphthalimide (27 g.), the mixture was refluxed for 2 hours and most of the alcohol removed by distillation. The product, isolated after the addition of water, crystallised from alcohol (20 c.c.) (charcoal) in rhombohedra (yield, 12—16 g.). This pale brown material is sufficiently pure for many purposes and one recrystallisation from alcohol gives the pure nitrile, m. p. 81°. The substance has been previously obtained by Gabriel (*Ber.*, 1889, **22**, 3337) from potassium phthalimide and γ-bromobutyronitrile.

3-Phenylindole-2-carboxylic Acid (formula as V).—The phenylhydrazone of phenylpyruvic acid (Wislicenus, *Ber.*, 1887, **20**, 593) may be conveniently prepared by the following application of the Japp-Klingemann reaction. A solution of sodium hydroxide (12 g.) in water (30 c.c.) was added to one of ethyl α-acetyl-β-phenylpropionate (22 g.) in alcohol (150 c.c.) and, without delay, a solution of benzenediazonium chloride (from 9·3 g. of aniline and 50 c.c. of concentrated hydrochloric acid) was introduced, causing the precipitation of a heavy brown oil. A few minutes later the product was precipitated by the addition of water, washed by decantation, and, as it did not solidify, was at once hydrolysed by means of alcoholic sodium hydroxide on the steam-bath. The acid obtained on acidification was crystallised from aqueous alcohol, yielding 20 g. of a product, m. p. 160° (Wislicenus, *loc. cit.*, gives m. p. 161°).

A solution of the hydrazone (26 g.) in alcohol (75 c.c.) was rapidly saturated with hydrogen chloride and then refluxed for ½ hour; ammonium chloride separated. The resinous mass obtained on the addition of water afforded, on solution in hot alcohol and cooling, about 2 g. of *ethyl 3-phenylindole-2-carboxylate* (V). This ester crystallised from alcohol in colourless rhombohedra, m. p. 137—138° (Found: C, 76·8; H, 5·8; N, 5·3. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7; N, 5·3%). The alcoholic mother-liquor, after the separation of the ester, was made strongly alkaline by means of sodium hydroxide and heated on the steam-bath for an hour. Water then precipitated some 3-phenylindole, identified by its m. p. (87°) and by colour reactions, whilst the alkaline filtrate from this, on acidification, gave *3-phenylindole-2-carboxylic acid*, which was dried (10 g.) and crystallised from benzene. The colourless clusters of needles, m. p. 186° (Found: C, 75·3; H, 4·7; N, 5·8. $C_{15}H_{11}O_2N$ requires C, 75·9; H, 4·6; N, 5·9%), lose carbon dioxide, on heating, with formation of 3-phenylindole.

α-Phenylbutane-βγ-dione β-Phenylhydrazone (VI).—A solution of sodium hydroxide (9 g.) in water (25 c.c.) was added to ethyl α-acetyl-β-phenylpropionate (44 g.) in alcohol (50 c.c.). Shortly after the formation of a semi-solid gelatinous mass, water (500 c.c.) was added and the mixture stirred until only a small amount of oil remained unacted upon. This was removed by passing the liquid through a wet filter and a solution of benzenediazonium chloride (from 18 g. of aniline, 13 g. of sodium nitrite, and 50 c.c. of concentrated hydrochloric acid) was introduced. The addition of crystallised sodium acetate (100 g.) caused the rapid precipitation of the phenylhydrazone, which was carried to the surface by the liberated carbon dioxide and was collected, washed with water, aqueous sodium carbonate, and then again with water (yield after drying, 42—44 g.). The substance, which may be distilled in small quantities undecomposed under diminished pressure, crystallises from alcohol or benzene in glistening, pale yellow plates, m. p. 108°, and is readily soluble in chloroform (Found: C, 75·5; H, 6·3; N, 11·2. $C_{16}H_{16}ON_2$ requires C, 76·2; H, 6·3; N, 11·1%).

α-Phenylbutane-βγ-dione β-m-*nitrophenylhydrazone* and β-2:5-*dimethoxyphenylhydrazone* were obtained in the same way as the preceding compound, the appropriate derivative being substituted for aniline. The former is sparingly soluble in acetic acid, from which it separates in yellow needles, m. p. 146° (Found: C, 64·9; H, 5·1; N, 14·5. $C_{16}H_{15}O_3N_3$ requires C, 64·6; H, 5·0; N, 14·1%). The latter crystallises from alcohol in greenish-yellow needles, m. p. 107° (Found: C, 69·5; H, 6·5; N, 9·2. $C_{18}H_{20}O_3N_2$ requires C, 69·2; H, 6·4; N, 9·0%). In both cases, the yield was 80% of that theoretically possible.

2-Acetyl-3-phenylindole (VII).—α-Phenylbutane-βγ-dione β-phenylhydrazone (25·2 g.) was added in one portion to boiling hydrochloric acid (75 c.c.; *d* 1·16), and the mixture then boiled for 15 minutes. The oil precipitated on the addition of a large volume of water was washed by decantation and soon crystallised (dried, 23 g.). The substance was crystallised from alcohol and then from benzene, being obtained in stout, pale yellow prisms, m. p. 151° (Found: C, 81·4; H, 5·8; N, 6·1. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0%). The crude product may also be conveniently purified by distillation under diminished pressure. On fusion with sodium hydroxide and a little water for a few minutes at a high temperature, 3-phenylindole was obtained; it was identified by the m. p. (87°) of a mixture and by comparison with an authentic specimen.

Ethyl δ-*Phthalimido*-α-*acetylvalerate*.—This ester has been described by Gabriel (*loc. cit.*). Since relatively large quantities of it were required, we have studied the optimum conditions for the preparation. After sodium (24 g.) had been dissolved in anhydrous alcohol (300 c.c.), ethyl acetoacetate (140 g.) and γ-bromopropylphthalimide (268 g.) (Gabriel and Weiner, *Ber.*, 1888, **21**, 2671; compare Ing and Manske, this vol., p. 2348) were successively introduced and the mixture was refluxed for 2 hours. The greater part of the alcohol was then removed by distillation and the residue added to water (2000 c.c.). The oil crystallised and was collected, washed with much cold water and dried. The yield was uniformly 300—310 g. and in this form the substance is sufficiently pure to be employed for the purposes mentioned below. A specimen crystallised from benzene–light petroleum had m. p. 64° (Gabriel, *loc. cit.*, gives 65°) (Found: C, 64·8; H, 6·0; N, 4·3. Calc. for $C_{17}H_{19}O_5N$: C, 64·4; H, 6·0; N, 4·4%).

ζ-o-*Carboxybenzamidohexane*-βγ-*dione* γ-*Phenylhydrazone* (VIII).—A solution of sodium hydroxide (25 g.) in water (100 c.c.) was added to one of ethyl δ-phthalimido-α-acetylvalerate (95 g.) in alcohol (100 c.c.), the temperature being kept below 10°. After 5 hours, cold water (1000 c.c.) was added and on the following day the solution was shaken with a little animal charcoal and filtered, and crystallised sodium acetate (200 g.) was dissolved in it. The liquid was then mechanically agitated during the introduction of a solution of benzenediazonium chloride prepared from aniline (28 g.), concentrated hydrochloric acid (150 c.c.), and sodium nitrite (21 g.) dissolved in water (50 c.c.). A brown, pasty mass was immediately formed and carried to the surface by the liberated carbon dioxide. Stirring was continued for an hour and after the solution had been rendered strongly acid by means of hydrochloric acid the pale brown precipitate was collected and washed with water. The crude product was dissolved as far as possible in aqueous sodium hydroxide (1000 c.c. of 4%) and was reprecipitated after the solution had been treated with charcoal and filtered (dried, 90—95 g.). After crystallisation from acetone, almost colourless needles, melting with loss of water at 156—157°, were obtained (Found: C, 65·4; H, 6·1; N, 11·3. $C_{20}H_{21}O_4N_3$ requires C, 65·4; H, 5·7; N, 11·4%). This acid is sparingly soluble in most organic solvents in the cold.

ζ-Phthalimidohexane-βγ-dione γ-Phenylhydrazone (IX).—The acid just described was at first converted into an anhydro-derivative by heating it at 180° under diminished pressure (yield, 10—20%). The following procedure is much more satisfactory, the yield being 70% of that theoretically possible. Carboxybenzamidohexanedione phenylhydrazone (37 g.) was added to an equal weight of boiling, freshly-distilled acetic anhydride, and the source of heat removed. When the exothermic reaction ceased, the mixture was boiled for 5 minutes, allowed to cool to 80°, and 95% alcohol (40 c.c.) then added. Crystallisation was induced by inoculation and after cooling in ice-water the solid was collected and washed with alcohol until the filtrate was colourless (dried, 24—28 g.). This material, m. p. 168—170°, is pure enough for most purposes. The substance crystallises from acetic acid in pale yellow needles, m. p. 172° (Found: C, 68·7; H, 5·7; N, 11·5. $C_{20}H_{19}O_3N_3$ requires C, 68·8; H, 5·4; N, 12·0%). It is but sparingly soluble in hot acetic acid and extremely sparingly soluble in boiling alcohol.

5-Keto-6-methyl-2 : 3 : 4 : 5-tetrahydropyridine 5-Phenylhydrazone (X).—A stream of dry hydrogen chloride was led during 10 minutes through a boiling solution of carboxybenzamidohexanedione phenylhydrazone (37 g.) in acetic acid (75 c.c.). The hydrochloride which separated on cooling was collected and washed with cold acetic acid (dried, 20 g.). The corresponding base, set free by means of aqueous sodium hydroxide, crystallised from benzene in pale yellow, almost rectangular prisms, m. p. 134—135°, which effloresce on exposure to air and even then contain benzene (Found: C, 74·9; H, 7·7; N, 17·7. $C_{12}H_{15}N_3,\frac{1}{2}C_6H_6$ requires C, 75·0; H, 7·5; N, 17·5%); it is readily soluble in alcohol, moderately readily soluble in benzene, and sparingly soluble in light petroleum. The *hydrochloride* is sparingly soluble in water and crystallises in brilliant yellow leaflets, m. p. 286° (decomp.) (Found: C, 61·7; H, 7·1; N, 17·6; Cl, 14·7. $C_{12}H_{15}N_3,HCl$ requires C, 60·6; H, 6·8; N, 17·7; Cl, 14·9%). The solutions of this salt and of other salts of the base and of the analogues described below are bright yellow and unaffected by nitrous acid. Addition of zinc dust to an acid solution causes decoloration and a diazotisable amine is produced. The filtrate from the original preparation contained phthalic acid but no ammonium salt. Owing to the unusual difficulty experienced in getting satisfactory or consistent results in the estimation of carbon, two further examples of the reaction were investigated and the combined evidence as to the composition of these curious bases is decisive.

ζ-o-*Carboxybenzamidohexane-βγ-dione* γ-m-*Chlorophenylhydrazone* (formula as VIII).—This substance was obtained in the same way as the corresponding phenylhydrazone on substituting *m*-chloroaniline for aniline. The crude product was purified by reprecipitation from a solution in dilute aqueous sodium hydroxide, and the substance separated from acetone and then from alcohol as a pale yellow, crystalline powder, m. p. 210° (decomp.) (Found: C, 60·4; H, 5·2; N, 10·5; Cl, 8·5. $C_{20}H_{20}O_4N_3Cl$ requires C, 59·7; H, 5·0; N, 10·4; Cl, 8·8%). This acid is sparingly soluble in most organic solvents.

5-*Keto-6-methyl-2 : 3 : 4 : 5-tetrahydropyridine* 5-m-*Chlorophenylhydrazone* (formula as X).—Carboxybenzamidohexanedione chlorophenylhydrazone (10 g.), dissolved in boiling acetic acid (20 c.c.), was submitted to the action of a stream of hydrogen chloride for 5 minutes, the resulting hydrochloride crystallising, even from the hot solution. The related base, isolated from an aqueous solution which had been treated with charcoal (yield, 5 g.), crystallised from benzene in yellow prisms, m. p. 161° (Found: N, 17·7; Cl, 14·6. $C_{12}H_{14}N_3Cl$ requires N, 17·8; Cl, 15·1%). The *hydrochloride* separates from boiling aqueous solutions in glistening, yellow leaflets.

5-*Keto-6-phenyl-2 : 3 : 4 : 5-tetrahydropyridine* 5-*Phenylhydrazone* (formula as X).—In the preparation of this substance no serious attempt was made to purify the intermediates. The condensation of ethyl benzoylacetate (39 g.) and γ-bromopropylphthalimide (52 g.) in the presence of alcoholic sodium ethoxide gave 74 g. of an oily product which was hydrolysed by means of aqueous-alcoholic sodium hydroxide and subsequently coupled with benzenediazonium chloride as in the type example. The yield of resinous hydrazone acid was 60 g. A stream of hydrogen chloride was passed into a solution of one-third of this product in its own weight of boiling acetic acid for 10 minutes. On cooling, a certain amount of the hydrochloride separated, but it was found advantageous to add water (200 c.c.), boil (charcoal), and concentrate the filtered solution to about 75 c.c. On cooling, there was a copious separation of a pale yellow, crystalline *hydrochloride*, which was collected, washed, and then decomposed with aqueous sodium hydroxide. The base (5 g.) crystallised from benzene–methyl alcohol in yellow, prismatic needles, m. p. 146—147° (Found: C, 78·2; H, 6·9; N, 15·2. $C_{17}H_{17}N_3$ requires C, 77·6; H, 6·5; N, 15·9%).

2-*Acetyl*-3-β-*phthalimidoethylindole* (XI).—The indole cyclisation of phthalimidohexanedione phenylhydrazone does not give quite satisfactory yields under any conditions which we have employed, but the following procedure affords uniform results. A stream of dry hydrogen chloride was passed through a suspension of the hydrazone (17·5 g.) in boiling alcohol (150 c.c.) (reflux) for 45 minutes. Most of the alcohol was removed by distillation and the residue repeatedly washed with hot water. The aqueous extract contained ammonium chloride. The brown tar was dried (17 g.) and refluxed with acetone (400 c.c.) and animal charcoal (2 g.) for about 2 hours; the solution was then filtered and concentrated to a small volume. On keeping for several days, the residual pale brown syrup became semi-solid—the change may be hastened by inoculation. The crystals were collected, washed with cold acetone, and dried (2·5—3 g.; m. p. 206—210°). The substance is very sparingly soluble in boiling acetone or alcohol and crystallises from acetic acid in small, colourless, rhombic prisms, m. p. 214° (Found: C, 72·5; H, 5·0; N, 8·4. $C_{20}H_{16}O_3N_2$ requires C, 72·3; H, 4·8; N, 8·4%). The combined mother-liquors from four such preparations were worked up for harman (see below).

Harmalan (XII).—A mixture of acetylphthalimidoethylindole with its own weight of hydrazine hydrate and ten times its weight of alcohol was boiled for 20 minutes and the resulting clear solution, acidified with hydrochloric acid, was boiled for a further 20 minutes and filtered through a layer of charcoal. An excess of sodium hydroxide was added to the pale yellow, strongly fluorescent filtrate, and, after cooling, the semi-crystalline base was collected, washed, and dried (weight about ½ of the phthalimido-derivative taken). Harmalan crystallises best from water or from 10% alcohol in very pale yellow needles and after two recrystallisations has m. p. 182—183°, if previously dried for several hours at 75°. This product lost 48·9% at 100° in a vacuum (Found in anhydrous material: C, 78·1; H, 6·6; N, 14·8. $C_{12}H_{12}N_2,10H_2O$ requires H_2O, 49·4%. $C_{12}H_{12}N_2$ requires C, 78·3; H, 6·5; N, 15·2%). Solutions of salts of harmalan are pale yellow and exhibit a blue fluorescence, which is intensified on the addition of alcohol. The solution in concentrated sulphuric acid is non-fluorescent.

Harman (XIII).—Harmalan chromate is a sparingly soluble, brown powder and on boiling with dilute sulphuric acid some harman is produced, although the yield is poor. Harman has been prepared in this way from pure harmalan, but a larger quantity became available from residues. The mother-liquors obtained in the preparation of acetylphthalimidoethylindole were freed from acetone on the steam-bath and the tar was extracted with boiling alcohol (150 c.c.). After several days, the alcohol was decanted, the resin mixed with hydrazine hydrate (25 g.) and refluxed for 1 hour with alcohol (100 c.c.), and the resulting solution diluted with water (500 c.c.), filtered (charcoal), and acidified. The precipitated phthalhydrazide was removed (charcoal again), and the pale brown filtrate rendered strongly alkaline by the addition of sodium hydroxide. The precipitated base (about 7 g.) was collected, dissolved in dilute sulphuric acid, and a slight excess of sodium dichromate added to the solution, which was then boiled for several hours. The sparingly soluble chromate gradually disappeared as oxidation proceeded. The liquid was rendered alkaline by means of sodium hydroxide and filtered hot, and the residue extracted thrice with boiling water. The combined filtrate and extracts deposited, on cooling, sand-coloured needles, m. p. 210—215° (about 1·0 g.). One crystallisation from 5% alcohol raised the m. p. to 237°, which is the m. p. of harman (Hopkins and Cole, *J. Physiol.*, 1903, **29**, 451, give 238° as the m. p. of the base, $C_{12}H_{10}N_2$, subsequently shown to be harman; compare also Perkin and Robinson, J., 1919, **115**, 967, and Späth, *Monatsh.*, 1919, **40**, 351, who give 238° and 237—238°, respectively) (Found: N, 15·0. Calc. for $C_{12}H_{10}N_2$: N, 15·3%). The base exhibited the characteristic properties of harman, in particular the bluish-violet fluorescence of the aqueous solutions of its salts.

ζ-o-Carboxybenzamidohexane-βγ-dione β-m-Methoxyphenylhydrazone (formula as VIII).—A solution of sodium δ-*o*-carboxybenzamido-α-acetylvalerate, obtained exactly as described above from ethyl δ-phthalimido-α-acetylvalerate (95 g.), in which crystallised sodium acetate (200 g.) had been dissolved was stirred, and a solution of *m*-methoxybenzenediazonium chloride (from 37 g. of *m*-anisidine, 150 c.c. of concentrated hydrochloric acid, and 21 g. of sodium nitrite) gradually introduced. The precipitated brown semi-solid hydrazone adhered to the sides of the vessel and was washed by decantation and dried (95—100 g.). The substance was employed in this form for the next stage. It may be purified by solution in aqueous sodium carbonate (charcoal) and reprecipitation; crystallised from much ethyl acetate and again from alcohol, it then forms orange-yellow plates, m. p. 208° (decomp.) (Found: C, 63·8; H, 5·9; N, 10·6. $C_{21}H_{23}O_3N_3$ requires C, 63·5; H, 5·8; N, 10·6%).

ζ-Phthalimidohexane-βγ-dione γ-m-Methoxyphenylhydrazone (XIV). —The above hydrazone acid (crude product, 40 g.) was added to boiling acetic anhydride (40 g.) and the solution was boiled for

5 minutes and then allowed to cool to about 80°. Alcohol (40 c.c.) was added and, on cooling and keeping, the mixture deposited a mass of crystals which were collected, washed with alcohol, and dried (28 g.; m. p. 163—165°). The substance crystallises from acetic acid in orange prisms, m. p. 167—168° (Found: C, 66·1; H, 5·6; N, 11·3. $C_{21}H_{21}O_4N_3$ requires C, 66·5; H, 5·5; N, 11·1%), and is readily soluble in chloroform.

6-*Methoxy-2-acetyl-3-β-phthalimidoethylindole* (XV).—After numerous unsuccessful attempts to prepare this indole derivative, it was found that the following procedure gave results which were at least as good as those obtained in the simpler case. A stream of hydrogen chloride was passed through a boiling solution of phthalimidohexanedione *m*-methoxyphenylhydrazone (18 g.) in *n*-butyl alcohol (150 c.c.) for 15 minutes. The solvent was then removed by distillation under diminished pressure and the brown, resinous residue was freed from impurities volatile in a current of steam. The heavy oil was repeatedly washed with hot water, dried at 100°, and treated with animal charcoal in boiling acetone solution (600 c.c.) for several hours. The filtered liquid, concentrated to a small volume, deposited the indole in the course of a few hours in almost colourless crystals (2·4 g.; m. p. 214°). The substance crystallises from acetic acid in colourless prisms, m. p. 218° (Found: C, 69·1; H, 5·2; N, 7·7. $C_{21}H_{18}O_4N_2$ requires C, 69·6; H, 5·0; N, 7·7%). Further small quantities of the substance may be obtained from the mother-liquor by renewed solution in acetone, treatment with charcoal, and concentration to a small volume.

Harmaline (II).—The removal of the phthalic residue from methoxyacetylphthalimidoethylindole was effected by the action of hydrazine as described in the section dealing with the preparation of harmalan. Harmaline, precipitated by the addition of sodium hydroxide to the acid solution, was obtained in 90% yield. Crystallisation from methyl alcohol with the aid of charcoal gave the pure base which, alone or intimately mixed with a specimen of the alkaloid derived from *Peganum harmala*, melted at 239—240° (Found in the synthetic specimen: C, 73·1; H, 7·0; N, 12·7. Calc. for $C_{13}H_{14}ON_2$: C, 72·9; H, 6·5; N, 13·1%). Comparison of the crystalline forms and fluorescent properties confirmed the identity of the specimens and nothing was observed which could differentiate them. The synthetic base was acetylated (O. Fischer, *Ber.*, 1897, **30**, 2484) and the acetyl derivative, after two crystallisations from alcohol, had m. p. 204°, alone or mixed with an authentic specimen from natural harmaline. It displayed the characteristic colour changes on heating in alcoholic aqueous hydrochloric acid solution.

Harmine (I).—In the course of the work, partly in preliminary experiments, but chiefly by working up the mother-liquors from the indole derivative preparation with hydrazine hydrate, several grams of impure and uncrystallisable harmaline were accumulated. This material was oxidised by means of chromic acid in boiling dilute sulphuric acid solution and the resulting harmine could then be crystallised from methyl alcohol with the aid of charcoal. The pale yellow needles (Found: N, 13·2. Calc. for $C_{13}H_{12}ON_2$: N, 13·3%) had m. p. 256—258°, alone or mixed with an authentic specimen of harmine, and careful comparison with the natural base also showed that the specimens were identical.

We desire to thank the Royal Commissioners for the Exhibition of 1851 for a scholarship which enabled one of us to take part in the investigation and we are also indebted to the Chemical Society for a grant which defrayed a part of the expenses incurred.

THE UNIVERSITIES OF OXFORD AND
MANCHESTER.

[*Received, November 15th*, 1926.]

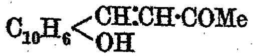
II.—*Styrylpyrylium Salts. Part VIII. 3-Styryl Derivatives of β-Naphthapyrylium Chloride.*

By ROBERT DICKINSON and ISIDOR MORRIS HEILBRON.

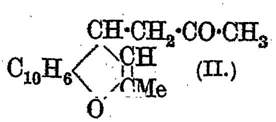
IN continuation of previous work, a study has been made of the styryl derivatives of β-naphthapyrylium chloride.

We were unable to prepare them by a method analogous to that used by Buck and Heilbron (J., 1922, 121, 1198), since the condensation of 2-naphthol-1-aldehyde with acetone in the presence of alkali failed to give the expected β-2-hydroxy-1-naphthylvinyl methyl ketone (I). The only pure product isolated was 1-*acetonyl*-3-*methyl*-1 : 4-β-*naphthapyran* (II), which was obtained in poor yield, the bulk of the reaction product being an amorphous, yellow solid which resisted all attempts at purification.

(I.)



$$C_{10}H_6<\begin{matrix}CH{:}CH\cdot COMe\\ OH\end{matrix}$$

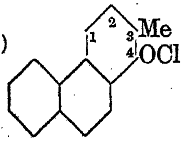


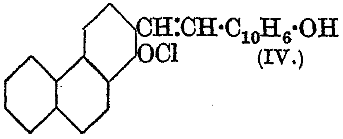
$$C_{10}H_6\left<\begin{matrix}CH\cdot CH_2\cdot CO\cdot CH_3 & \\ & CH\\ & \|\\ & CMe\\ O & \end{matrix}\right.$$

(II.)

Attempts were next made to prepare 3-methyl-β-naphthapyrylium chloride (III) with a view to condensing it further with aromatic aldehydes to the styryl derivatives (compare Buck and Heilbron, J., 1923, 123, 2521), but this method failed because the condensation of 2-naphthol-1-aldehyde with acetone in acid solution gave solely 3-(β-2′-*hydroxy*-1′-*naphthylvinyl*)-β-*naphthapyrylium chloride* (IV).

(III.)

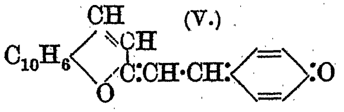




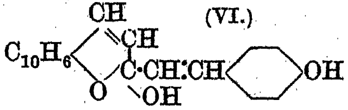
(IV.)

The salts were ultimately obtained in good yield by the condensation of 2-naphthol-1-aldehyde with styryl methyl ketones by means of dry hydrogen chloride—a somewhat unexpected result, since the corresponding condensation for styrylbenzopyrylium salts was unsatisfactory (Buck and Heilbron, J., 1922, **121**, 1198).

The styryl-β-naphthapyrylium salts are highly coloured, crystalline compounds closely resembling the 2-styrylbenzopyrylium salts in properties. For example, 3-p-*hydroxystyryl*-β-*naphthapyrylium chloride* gives a red aqueous solution which, on high dilution, becomes purplish-blue, and then, with a trace of sodium bicarbonate, cornflower-blue, and finally almost colourless. As in other similar cases, we attribute the colour change from red to blue, which is displayed only by those salts having a free hydroxyl in the 4′-position, to the formation of the quinonoid anhydro-base (V), which then hydrates to the colourless carbinol base (VI).



(V.)



(VI.)

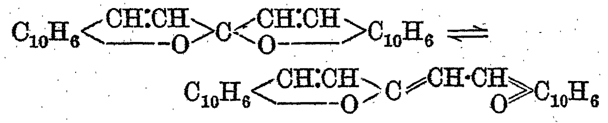
The view that the similar colour changes observed in the anthocyanidin series of salts are due to the same structural rearrangements (Buck and Heilbron, J., 1922, **121**, 1203) has been criticised by Willstätter and Schmidt (*Ber.*, 1924, **57**, 1945) as failing to account for the reactions of malvidin and œnidin chlorides, both of which, according to Willstätter, contain methoxyl groups in the 4′-position (*Annalen*, 1915, **408**, 83, 122). Such formulations are, however, supported neither by Gatewood and Robinson in the case of malvidin (J., 1926, 1959) nor by Anderson and Nabenhauer for œnidin (*J. Amer. Chem. Soc.*, 1926, **48**, 2997).

All the styryl-β-naphthapyrylium salts, on treatment with aqueous sodium hydroxide, give colourless solutions which slowly become intensely red. This colour change, which may possibly be due to fission of the pyrylium ring, is being investigated.

The parent substance, 3-*styryl*-β-*naphthapyrylium chloride*, is interesting in that Buck and Heilbron (*loc. cit.*) were unable to prepare the corresponding benzopyrylium salt, and further because it differs from its derivatives : its colour in water is bright orange, and solutions in water, alcohol, and concentrated sulphuric acid all show a remarkably intense greenish-yellow fluorescence; this property is only exhibited by its derivatives in the last solvent.

3-(β-2′-Hydroxy-1′-naphthylvinyl)-β-naphthapyrylium chloride (IV) is readily changed by water, added to an alcoholic solution, or by sodium acetate into the colourless *di-β-naphthaspiropyran* (VII).

(VII.)



$$C_{10}H_6<\frac{CH:CH}{-O}>C<\frac{CH:CH}{O-}>C_{10}H_6 \rightleftharpoons$$

$$C_{10}H_6<\frac{CH:CH}{-O}>C{=}\frac{CH\cdot CH}{O}{\geqslant}C_{10}H_6$$

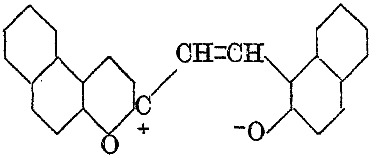
(VIII.)

A remarkable property of this compound is its behaviour in high-boiling solvents. Its colourless solution in nitrobenzene or xylene develops, at about 100°, a purple colour which becomes progressively deeper and more intense as the temperature rises; on cooling, the reverse phenomena are observed. These changes may be repeated any number of times without the least sign of permanent decomposition. Although this behaviour resembles that accompanying the decomposition of hexa-aryl ethanes and of certain phenolic peroxides into free radicals (compare Gomberg, *Chemical Reviews*, 1925, **1**, 91), a similar decomposition does not take place here, molecular-weight determinations at high temperatures giving normal values. It is tentatively suggested that the purple colour may be due to a change in the valency distribution (VII ⇌ VIII). The possibility of both pyran rings opening in a similar manner has not been overlooked, but is regarded as unlikely.

On boiling with alcoholic potash, di-β-naphtha*spiro*pyran gradually gives a blood-red solution, probably owing to formation of the potassium salt of the corresponding dinaphthylvinyl ketone. An examination of this question and a study of other similarly constituted spiropyrans are now in progress.

Since the completion of this work a communication has appeared by Löwenbein and Katz (*Ber.*, 1926, **59**, 1377) dealing with the preparation of certain 2-aryl derivatives of (IV) obtained by the condensation of 2-naphthol-1-aldehyde with α-arylacetoacetic esters. These compounds also yield di-β-naphtha*spiro*pyrans analogous to (VII), all of which exhibit similar colour changes in high-boiling solvents. The conclusions arrived at by these authors to account for the phenomenon are wholly in harmony with the views expressed above.

Dilthey and Wizinger (*Ber.*, 1926, **59**, 1856) announce in a preliminary notice that they also have prepared di-β-naphtha*spiro*pyran, but no details of their method are available. These authors, who have approached the problem from another direction, regard the coloured form as a dipolar anhydride (IX) of the normal *spiro*pyran.



(IX.)

EXPERIMENTAL.

1-*Acetonyl*-3-*methyl*-1 : 4-β-*naphthapyran* (II).—2-Naphthol-1-aldehyde (5 g.) (Fosse, *Bull. Soc. chim.*, 1901, 25, 371) was dissolved in a mixture of alcohol and acetone (20 c.c. of each) and treated with 50% potassium hydroxide (8 c.c.). The mixture was gently heated under reflux for 3 hours, and after cooling, the blood-red liquid was extracted with ether. The ethereal solution was washed, dried, and concentrated, whereupon a small quantity of a crystalline solid separated. The remainder of the extract consisted of an unworkable brown resin. After three recrystallisations from alcohol, the solid was obtained in faintly yellow, fern-like aggregates, m. p. 152—153°. The compound, which is insoluble in water and aqueous sodium hydroxide, gives no coloration with alcoholic hydrogen chloride and only slowly absorbs bromine, hydrogen bromide being evolved (Found: C, 80·6; H, 6·3. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·35%).

After removal of dissolved ether by a current of warm air, the blood-red aqueous liquid, on saturation with either carbon dioxide or dilute hydrochloric acid, deposited a yellow solid which, on drying, became dull olive-green. By repeated precipitation from benzene or ethyl acetate by addition of light petroleum, it was obtained as an amorphous, yellow powder, melting above 250° and insoluble in aqueous alkali.

Derivatives of 3-*Styryl*-β-*naphthapyrylium Chloride.*—These salts were all prepared by the same general method—saturation of an alcoholic solution of 2-naphthol-1-aldehyde and the requisite styryl methyl ketone with hydrogen chloride. The styryl ketone was always used in slight excess, in order to avoid the formation of di-β-naphthapyrylium chloride (Betti and Mundici, *Atti R. Accad. Lincei*, 1904, v, **13**, ii, 542; *Gazzetta*, 1905, **35**, ii, 46). It was found advantageous to condense small amounts of material at a time, otherwise the product either failed to separate or was only obtained in small yield. As is the case with the corresponding benzopyrylium chlorides, formic acid was found to be the best crystallising medium, ether being added to reduce the solubility. No melting points are recorded for these salts, as on heating they gradually decompose and pass into tars.

3-*Styryl*-β-*naphthapyrylium chloride* was prepared as above from styryl methyl ketone (Knoevenagel, *Annalen*, 1914, **402**, 111) and 2-naphthol-1-aldehyde. The salt separated from formic acid, containing about 60% of anhydrous ether, in centimetre-long, thin plates which appeared blood-red in transmitted light and showed a pronounced beetle-green reflex. It is moderately easily soluble in water to an orange-yellow solution, readily so in alcohol or acetone to a deep orange liquid; in concentrated sulphuric acid the colour is orange-red. All the solutions have an intense greenish-yellow fluorescence (Found: C, 72·5; H, 4·9; Cl, 9·6. $C_{21}H_{15}OCl,HCO_2H$ requires C, 72·4; H, 4·7; Cl, 9·7%).*

3-p-*Hydroxystyryl*-β-*naphthapyrylium chloride*, prepared from *p*-hydroxystyryl methyl ketone (Buck and Heilbron, J., 1922, **121**, 1101), forms glistening, dark olive-green prisms, which are deep violet by transmitted light (under the microscope). The salt is slightly soluble in water to a cherry-red solution, which on dilution passes through violet to almost pure blue, the change being completed by addition of a drop of dilute sodium bicarbonate solution. The blue solutions slowly fade until they are almost colourless (10—15 minutes). With dilute aqueous sodium hydroxide, the blue colour persists for a few seconds only, after which a red colour, resembling that of the parent chloride, gradually develops. The salt dissolves in concentrated sulphuric acid to a reddish-orange liquid with an intense greenish-orange fluorescence (Found: C, 68·1; H, 4·6; Cl, 9·6. $C_{21}H_{15}O_2Cl,2H_2O$ requires C, 68·0; H, 5·1; Cl, 9·6%).

3-3′-*Methoxy*-4′-*hydroxystyryl*-β-*naphthapyrylium chloride*, prepared from 3-methoxy-4-hydroxystyryl methyl ketone (McGookin and Sinclair, J., 1926, 1578), forms aggregates of dull green needles, sparingly soluble in water to a pink solution. In alcohol the colour is bluish-purple, becoming purplish-red on addition of a little water. In its behaviour with water and alkalis it closely resembles the *p*-hydroxy-analogue. In concentrated sulphuric acid, it gives a red solution with a dark red fluorescence (Found: C, 65·8; H, 4·9; Cl, 8·9. $C_{22}H_{17}O_3Cl,2H_2O$ requires C, 65·9; H, 5·2; Cl, 8·9%).

3-p-*Methoxystyryl*-β-*naphthapyrylium chloride*, prepared from *p*-methoxystyryl methyl ketone (Baeyer and Villiger, *Ber.*, 1902, **35**, 1189), separates in prisms resembling the *p*-hydroxy-analogue but also showing a faint golden reflex. It is soluble in alcohol to a deep purplish-red solution with an intense red fluorescence, which disappears on addition of water. Its aqueous solution in high dilution is pink, which slowly fades to pale yellow, a slight opalescence being also present. In concentrated sulphuric acid, the solution is orange-red with a fluorescence similar to that of the *p*-hydroxy-compound (Found: C, 66·9; H, 5·2; Cl, 8·7. $C_{22}H_{17}O_2Cl,HCO_2H,H_2O$ requires C, 66·9; H, 5·1; Cl, 8·6%).

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* All halogen estimations were carried out by Stepanoff's method (*Ber.*, 1906, **39**, 4056) as modified by van Duin (*Rec. trav. chim.*, 1926, **45**, 343).

3-3′ : 4′-*Dimethoxystyryl*-β-*naphthapyrylium chloride*, prepared from 3 : 4-dimethoxystyryl methyl ketone (Kaufmann and Radosević, *Ber.*, 1916, 49, 675), crystallises in dark green prisms with a bronze reflex. In its properties it closely resembles the *p*-methoxy-analogue, except that its alcoholic solution does not fluoresce and in concentrated sulphuric acid the fluorescence is very weak (Found: C, 65·1; H, 5·3; Cl, 7·8. $C_{23}H_{19}O_3Cl,HCO_2H,H_2O$ requires C, 65·1; H, 5·2; Cl, 8·0%).

3-3′ : 4′-*Methylenedioxystyryl*-β-*naphthapyrylium chloride* was obtained as a felted mass of minute, dark green needles (Found: C, 64·6; H, 4·5; Cl, 8·4. $C_{22}H_{15}O_3Cl,HCO_2H,H_2O$ requires C, 64·7; H, 4·5; Cl, 8·3%).

3-p-*Dimethylaminostyryl*-β-*naphthapyrylium Perchlorate*.—A solution of *p*-dimethylaminostyryl methyl ketone (2·1 g.) and 2-naphthol-1-aldehyde (2 g.) in glacial acetic acid (20 c.c.) was saturated with dry hydrogen chloride, acetic acid (10 c.c.) and 60% perchloric acid (5 c.c.) were added, and the whole was kept over-night. The separated solid, after being washed with acetic acid and with ether, consisted of small, chocolate-brown needles with a steely blue reflex. On treatment with acetone, a minute amount dissolved, giving a bright green solution; the residue was converted into a mass of emerald-green needles. Both crystalline forms are very sparingly soluble in alcohol to greenish-blue solutions, which with water change to pure azure blue. The brown crystals probably contain some addendum, for on keeping over solid potassium hydroxide in an exsiccator they slowly become dark green. Neither form has been analysed, owing to the explosive character of the compound.

3-(β-2′-*Hydroxy*-1′-*naphthylvinyl*)-β-*naphthapyrylium Chloride* (IV).—A solution of 2-naphthol-1-aldehyde (5 g.) in alcohol (75 c.c.) and acetone (10 c.c.) was saturated with hydrogen chloride. The liquid, at first deep indigo-blue, finally exhibited pleochroism, being brownish-red in thick and olive-green in thin layers. After 12 hours, the crystalline deposit was collected and recrystallised in the usual way, being obtained as a felted mass of small, dark green needles. It is insoluble in water, and moderately easily soluble in alcohol to an indigo-blue solution. Hot water rapidly hydrolyses the compound to the *spiro*pyran. On keeping over solid potassium hydroxide, a continuous slow loss of hydrogen chloride takes place; the substance loses its crystalline form and is converted into a dirty, purplish-coloured, amorphous mass, which contains a small amount of chlorine even after 3 months' keeping in a vacuum. Analysis of the salt was carried out immediately the compound had lost all odour of formic acid (Found: C, 69·2; H, 5·1; Cl, 8·0. $C_{25}H_{17}O_2Cl,HCO_2H,H_2O$ requires C, 69·6; H, 4·7; Cl, 7·9%).

Di-β-*naphtha*spiro*pyran* (VII) was prepared from the foregoing pyrylium salt by two methods. (i) The salt was dissolved in alcohol, and water added to the warm solution. (ii) The chloride was heated with water and treated with sodium acetate to ensure complete hydrolysis. The resultant pale blue solid was twice recrystallised from xylene, separating in colourless, irregular, thin plates, with a pearly lustre, which darkened at 240° and became tarry at about 260°. The spiro*pyran* is insoluble in water, and only sparingly soluble in the usual low-boiling solvents. It is soluble in warm, high-boiling liquids such as xylene, phenetole, nitrobenzene, and naphthalene. When it is heated with such a solvent, a purple colour develops at about 100°, becoming progressively darker as the temperature rises. In phenol or glacial acetic acid, the solution is intensely coloured in the cold. Suspended in alcohol and treated with hydrogen chloride, the *spiro*pyran reverts to the original pyrylium salt. When it is boiled with aqueous-alcoholic sodium hydroxide, a pink colour develops, which changes to blood-red after several hours' refluxing. The carmine solution in concentrated sulphuric acid shows a dark red fluorescence (Found: C, 85·8; H, 4·7; *M*, ebullioscopic in nitrobenzene, 344, 352, 334. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%; *M*, 348).

We desire to record our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) which enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, October 27th,* 1926.]

III.—3-*Nitro-4-amino- and the* 3:4-*Dihalogenobenzaldehydes.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

THE substituted benzaldehydes described in this paper were required for an investigation of the colour and constitution of dyes of the triphenylmethane series. They were all prepared at first from 3-nitro-4-aminobenzaldehyde; later, however, by a modification of Erdmann's method (D.R.-P. 62180), the 4-halogeno-3-nitrobenzaldehydes were obtained from the 4-halogenobenzaldehydes by direct nitration.

The preparation of a mononitro-derivative of *p*-aminobenzaldehyde was patented by Kalle and Co. (D.R.-P. 89244), but Walther and Bretschneider (*J. pr. Chem.*, 1898, 57, 535) were unable to reproduce their result. Cohn and Springer (*Monatsh.*, 1903, 24, 87) obtained 3-nitro-4-acetamidobenzaldehyde by nitrating *p*-acetamidobenzaldehyde with a mixture of sulphuric and nitric acids, and converted it into 3-nitro-4-aminobenzaldehyde by hydrolysing it with concentrated hydrochloric acid. This method, however, gave in our hands a very poor yield of a mixture of products, and the nitration of *p*-acetamidobenzaldehyde was much improved by using diacetylorthonitric acid in acetic anhydride solution; in this case formation of *p*-acetamidobenzylidene diacetate preceded nitration. The acetate groups can be removed from 3-nitro-4-acetamidobenzylidene diacetate either separately or together.

The various melting points recorded by Cohn and Springer (*loc. cit.*) have been confirmed, and the constitutions of all the aldehydes described in this paper have been established by converting them into the corresponding benzoic acids by oxidation with neutral aqueous permanganate.

The yellow *leuco*-compound obtained by condensing 3-nitro-4-aminobenzaldehyde with diethylaniline in hydrochloric acid solution gives, on oxidation, a dye which imparts to wool a blue shade with a faint red tint. Since benzaldehyde, similarly treated, gives a brilliant green dye, the influence of substitution in the condensing aldehyde on the colour of the triphenylmethane dye appears to be pronounced and is being investigated.

EXPERIMENTAL.

3-*Nitro*-4-*aminobenzaldehyde*.

The initial material, *p*-aminobenzaldehyde, was prepared by Geigy's process (D.R.-P. 86874) from *p*-nitrotoluene (300 g.) and sodium disulphide in boiling alcohol. Three-quarters of the alcohol were recovered prior to steam distillation, which removed most (120 g.) of the *p*-toluidine simultaneously formed; the non-volatile *p*-aminobenzaldehyde was then extracted with ether.

The crude product was directly acetylated by suspension in water (200 c.c.) and treatment first with glacial acetic acid (200 c.c.), a red precipitate forming, and then gradually with acetic anhydride (160 c.c.); the reaction was completed by heating on the water-bath until the solid dissolved (30 min.). On pouring the mixture into ice-water (1500 c.c.) a yellow, crystalline solid separated, and more was obtained by making the filtrate just alkaline and adding sodium chloride. The total yield was 145 g. of a mixture of *p*-acetamidobenzaldehyde, aceto-*p*-toluidide, and a small quantity of *p*-aminobenzylidene-*p*-toluidine.

This mixture (135 g.) was heated slowly to 50° with 33% aqueous sodium bisulphite (400 c.c.) and water (200 c.c.) and cooled, the undissolved portion was well washed, and the combined filtrate and washings were treated with 20% aqueous sodium hydroxide as long as *p*-acetamidobenzaldehyde was precipitated. This substance was colourless when freshly prepared but became more and more yellow on keeping. It crystallised from water in prisms, m. p. 156° (Janse, *Rec. trav. chim.*, 1921, **40**, 285, gives m. p. 152°) (Found: N, 8·7. Calc.: N, 8·6%). The p-*nitrophenylhydrazone* separated from alcohol in deep orange needles, m. p. 264—265° (Found: N, 19·0. $C_{15}H_{14}O_3N_4$ requires N, 18·8%).

The insoluble portion of the above mixture, on fractional crystallisation from alcohol, gave p-*acetamidobenzylidene*-p-*toluidine* as the least soluble constituent; this was identified by comparison with a specimen, m. p. 187—188°, prepared from *p*-toluidine and *p*-acetamidobenzaldehyde (Found: N, 11·2. $C_{16}H_{16}ON_2$ requires N, 11·1%).

During the above operations, partial change of the *p*-aminobenzaldehyde into its amorphous, insoluble modification occurred, and this could only be acetylated by warming with acetic anhydride.

Nitration of p-*Acetamidobenzaldehyde*.—The aldehyde (30 g.) was obtained in small crystals by rapidly cooling a warm solution in acetic anhydride (75 c.c.) to 20°. Diacetylorthonitric acid (40 c.c.) was gradually added, the temperature not being allowed to exceed 40—50°. The crystals dissolved; after the addition of about 12 c.c. of diacetylorthonitric acid colourless plates of *p*-acetamidobenzylidene diacetate separated; these dissolved on further addition of the acid and remained in solution even on cooling. Nitration had not yet occurred, and numerous experiments have indicated the preliminary formation of this diacetate to be essential to smooth nitration. After the diacetylnitric acid had been added, the mixture was kept at 50° for 15 minutes, cooled, and poured into ice-water (400 c.c.) with vigorous stirring. After 2 hours, the 3-*nitro-4-acetamidobenzylidene diacetate* produced was filtered off, washed, and dried (yield, 45 g.). It gave no hydrazone and crystallised from alcohol in pale yellow leaflets, m. p. 114° (Found: N, 8·7. $C_{13}H_{14}O_7N_2$ requires N, 9·0%). It was easily soluble in alcohol or glacial acetic acid but sparingly soluble in chloroform.

Unlike *p*-acetamidobenzaldehyde, *p*-acetamidobenzylidene diacetate remains unchanged in colour on keeping. It melts at 170° (Blanksma, *Chem. Weekblad*, 1909, 6, 899, gives m. p. 166°) (Found: N, 5·5. Calc.: N, 5·3%).

Hydrolysis of 3-Nitro-4-acetamidobenzylidene Diacetate.—The diacetate (10 g.) was heated on the water-bath for 15 minutes with concentrated hydrochloric acid (25 c.c.). Separation of 3-*nitro-4-aminobenzaldehyde* from the cherry-coloured solution then began and was completed by the addition of water. The product was only slightly soluble in concentrated or dilute hydrochloric acid, cold alcohol, or glacial acetic acid; it deepened in colour from yellow through orange to old-gold on prolonged contact with hot hydrochloric acid, and crystallised from alcohol or water in orange needles, m. p. 191° (Cohn and Springer, *loc. cit.*, give m. p. 190·5—191°) (Found: N, 17·0. Calc.: N, 16·9%).

3-Nitro-4-acetamidobenzaldehyde was obtained when the diacetate (2 g.) was triturated with concentrated hydrochloric acid (10 c.c.) and the mixture was heated gradually to 40° until solution occurred, and then cooled rapidly and thrown into cold water (yield, 1·3 g.). It crystallised from hot water in pale yellow needles, m. p. 155° (Cohn and Springer, *loc. cit.*, give m. p. 155°) (Found: N, 12·9. Calc.: N, 13·4%). The p-*nitrophenylhydrazone* crystallises from alcohol in deep orange needles, m. p. 289—290° (Found: N, 20·6. $C_{15}H_{13}O_5N_5$ requires N, 20·5%).

3-*Nitro-4-aminobenzaldehyde*-p-*nitrophenylhydrazone* crystallises from glacial acetic acid in dark maroon needles, m. p. 270—272° (Found: N, 23·1. $C_{13}H_{11}O_4N_5$ requires N, 23·3%).

3-*Nitro-4-aminobenzaldoxime* crystallises from dilute alcohol in orange needles, m. p. 207°, and gives a deep red solution in aqueous sodium hydroxide (Found: N, 23·05. $C_7H_7O_3N_3$ requires N, 23·2%).

3-*Nitrobenzaldehyde-4-azo-β-naphthol* crystallises from glacial acetic acid in fine, crimson needles, m. p. 271° (Found: N, 13·2. $C_{17}H_{11}O_4N_3$ requires N, 13·6%). It is very slightly soluble in all the usual solvents and gives an insoluble, brick-red sodium salt.

Diazotisation of 3-Nitro-4-aminobenzaldehyde.—A solution of the aldehyde (4 g.) in warm 80% acetic acid (30 c.c.) was cooled, and to the paste of fine crystals thus obtained 20% aqueous sodium nitrite (10 c.c.) was added, followed gradually by concentrated hydrochloric acid (10 c.c.), the temperature being kept just below 20°. (Diazotisation takes place more readily at *ca.* 20° than at 0°, and without loss of nitrogen.) After the excess of nitrous acid had been destroyed by carbamide, the 4-halogeno-3-nitrobenzaldehydes were obtained by the usual Sandmeyer processes. The

4-chloro-compound could be obtained only in about 30% yield, probably owing to the formation of a diphenyl derivative, but 4-bromo- and 4-iodo-3-nitrobenzaldehydes were isolated in nearly quantitative amounts and almost pure.

The p-*Nitrophenylhydrazones of the 4-Halogeno-3-nitro- and 3 : 4-Dihalogeno-benzaldehydes.*

The *p*-nitrophenylhydrazones of the 4-halogeno-3-nitrobenzaldehydes are very sparingly soluble in the usual solvents and the conditions for their preparation described below must be carefully observed if they are to be obtained crystalline. When heated, they exhibit a colour change from orange to red at *ca.* 160° which is not reversed on cooling (compare Chattaway and Walker, J., 1924, 125, 1210). The *p*-nitrophenylhydrazones of the 3 : 4-dihalogenobenzaldehydes are much more soluble.

A solution of the aldehyde (0·1 g.) in cold alcohol (5 c.c.) is made faintly turbid by dilution with water and is then heated to boiling, and a solution of *p*-nitrophenylhydrazine (0·6 g.) in alcohol (3 c.c.) and glacial acetic acid (0·5 c.c.) at the same temperature is added. The crystalline product that separates immediately has a very sharp m. p. When the method of preparation described by Hodgson and Beard (J., 1925, 127, 880) is used, the product is non-crystalline and very sparingly soluble and has an indefinite m. p.

The 4-Halogeno-3-nitrobenzaldehydes.

4-Chloro-3-nitrobenzaldehyde forms colourless needles, m. p. 64·5°, from dilute alcohol (Erdmann, *loc. cit.*, gives m. p. 64·5°) (Found : Cl, 18·9. Calc. : Cl, 19·1%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 278—279° (Found : Cl, 11·1. $C_{13}H_9O_4N_4Cl$ requires Cl, 11·1%) and the *oxime* crystallises from alcohol in pale yellow needles, m. p. 146° (Found : Cl, 17·6. $C_7H_5O_3N_2Cl$ requires Cl, 17·7%).

4-Chloro-3-nitrobenzoic acid crystallises from dilute acetic acid in colourless prisms, m. p. 180—181° (Hübner, *Z. Chem.*, 1866, 6, 5, gives m. p. 178—180°) (Found : Cl, 17·5. Calc. : Cl, 17·6%).

4-Bromo-3-nitrobenzaldehyde separates from alcohol in pale yellow needles, m. p. 106° (Schöpff, *Ber.*, 1891, 24, 3775, gives m. p. 103°) (Found : Br, 33·8. Calc. : Br, 34·0%), and is very volatile in steam. The p-*nitrophenylhydrazone* forms yellow, micro-crystalline needles, m. p. 282—283° (Found : Br, 21·8. $C_{13}H_9O_4N_4Br$ requires Br, 21·9%), and the oxime crystallises from dilute alcohol in orange needles, m. p. 154° (Schöpff, *loc. cit.*, gives m. p. 145—146°) (Found : Br, 32·3. Calc. : Br, 32·5%).

4-Bromo-3-nitrobenzoic acid crystallises from dilute acetic acid in colourless, fern-like masses, m. p. 203° (Hübner, Philipp, and Ohly, *Annalen*, 1867, **143**, 248, give m. p. 199°) (Found: Br, 32·3. Calc.: Br, 32·5%).

4-*Iodo-3-nitrobenzaldehyde* is only very slowly volatile in steam. It is sparingly soluble in cold alcohol and crystallises from a hot solution in deep yellow needles, m. p. 141° (Found: I, 45·4. $C_7H_4O_3NI$ requires I, 45·8%). The p-*nitrophenylhydrazone* forms yellow, microcrystalline needles, m. p. 277—278° (decomp.) (Found: I, 30·5. $C_{13}H_9O_4N_4I$ requires I, 30·8%). The *oxime* forms pale yellow needles, m. p. 157°, from alcohol (Found: I, 43·5. $C_7H_5O_3N_2I$ requires I, 43·5%).

4-Iodo-3-nitrobenzoic acid crystallises from alcohol in yellow prisms, m. p. 213° (Glassner, *Ber.*, 1875, **8**, 562, gives m. p. 210°) (Found: I, 43·0. Calc.: I, 43·3%).

Preparation of the 4-Halogeno-3-nitrobenzaldehydes by Direct Nitration of the 4-Halogenobenzaldehydes.—The aldehyde (10 g.) is added gradually to a mixture of sodium nitrate (5·5 g.) and concentrated sulphuric acid (60 g.) kept at 15—20°, and the whole is then heated at 70° for 15 minutes, cooled, and poured on to ice; the yield is almost quantitative (compare Erdmann, *loc. cit.*).

The 3 : 4-Dihalogenobenzaldehydes.

These aldehydes were prepared from the 4-halogeno-3-nitrobenzaldehydes by the method already described (*J. Soc. Chem. Ind.*, 1926, **45**, 91T).

3 : 4-Dichlorobenzaldehyde crystallises from alcohol in colourless needles, m. p. 44° (Erdmann and Schwechten, *Annalen*, 1890, **260**, 72, give m. p. 44°) (Found: Cl, 40·3. Calc.: Cl, 40·5%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 276—277° (Found: Cl, 22·7. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9%), and the *oxime* colourless needles, m. p. 118—119°, from dilute alcohol (E. and S., *loc. cit.*, give m. p. 114—115°) (Found: Cl, 37·1. Calc.: Cl, 37·3%).

3 : 4-Dichlorobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 201—202° (Beilstein and Kuhlberg, *Annalen*, 1869, **152**, 232, give m. p. 201—202°) (Found: Cl, 36·9. Calc.: Cl, 37·1%).

4-*Chloro-3-bromobenzaldehyde* forms colourless needles, m. p. 70°, from alcohol (0·1460 g.; 0·2232 g.; 0·2210 g.*). The p-*nitrophenylhydrazone* forms orange needles, m. p. 273—274° (Found: N, 12·0. $C_{13}H_9O_2N_3ClBr$ requires N, 11·8%), and the *oxime* crystallises from dilute alcohol in colourless needles, m. p. 131° (Found : N, 5·8. $C_7H_5ONClBr$ requires N, 5·5%).

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* In this and in the other cases given later, the three quantities are, respectively, the weight of substance taken for analysis and the weights of mixed silver halides found and calculated.

4-Chloro-3-bromobenzoic acid separates from dilute acetic acid in colourless plates, m. p. 215—216° (Cohen and Raper, J., 1904, **85**, 1269, give m. p. 214°) (0·1180 g.; 0·1650 g.; 0·1657 g.).

4-*Chloro*-3-*iodobenzaldehyde* is very volatile in steam and separates from alcohol in colourless, spear-shaped crystals, m. p. 117° (0·1332 g.; 0·1846 g.; 0·1892 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 277—278° (decomp.) (Found : N, 10·6. $C_{13}H_9O_2N_3ClI$ requires N, 10·5%), and the *oxime* is obtained from dilute alcohol in colourless needles, m. p. 115—116° (Found : N, 5·1. C_7H_5ONClI requires N, 5·0%).

4-*Chloro*-3-*iodobenzoic acid* separates from dilute acetic acid in colourless plates, m. p. 216—217° (0·1412 g.; 0·1872 g.; 0·1892 g.).

3-*Chloro*-4-*bromobenzaldehyde* crystallises from alcohol in colourless needles, m. p. 52° (0·1098 g.; 0·1150 g.; 0·1157 g.). The p-*nitrophenylhydrazone* separates in orange needles, m. p. 272—273° (Found : N, 12·1. $C_{13}H_9O_2N_3ClBr$ requires N, 11·8%), and the *oxime* in colourless needles, m. p. 104°, from dilute alcohol (Found : N, 5·7. $C_7H_5ONClBr$ requires N, 5·5%).

3-Chloro-4-bromobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 219° (Cohen and Raper, J., 1904, **85**, 1262, give m. p. 218°) (0·1180 g.; 0·1652 g.; 0·1657 g.).

3 : 4-*Dibromobenzaldehyde* separates from alcohol in colourless needles, m. p. 75° (Found : Br, 60·7. $C_7H_4OBr_2$ requires Br, 60·6%). The p-*nitrophenylhydrazone* separates in orange needles, m. p. 270—274° (Found : Br, 39·9. $C_{13}H_9O_2N_3Br_2$ requires Br, 40·2%), and the *oxime* in colourless needles, m. p. 129°, from dilute alcohol (Found : Br, 57·1. $C_7H_5ONBr_2$ requires Br, 57·3%).

3 : 4-Dibromobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 233—234° (Hübner, *Annalen*, 1884, **222**, 184, gives m. p. 232—235°) (Found : Br, 50·4. Calc. : Br, 50·7%).

4-*Bromo*-3-*iodobenzaldehyde* is obtained from alcohol in thick, colourless prisms, m. p. 127° (0·1555 g.; 0·2134 g.; 0·2115 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 265° (decomp.) (Found : N, 9·5. $C_{13}H_9O_2N_3BrI$ requires N, 9·4%), and the *oxime* colourless needles, m. p. 141°, from dilute alcohol (Found : N, 4·6. C_7H_5ONBrI requires N, 4·3%).

4-*Bromo*-3-*iodobenzoic acid* crystallises from dilute acetic acid in colourless needles, m. p. 243—244° (0·1082 g.; 0·1052 g.; 0·1060 g.).

3-*Chloro*-4-*iodobenzaldehyde* is very volatile in steam and separates from glacial acetic acid in colourless needles, m. p. 70·5° (0·1066 g.; 0·1482 g.; 0·1515 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 261—262° (decomp.), from dilute alcohol (Found: N, 10·7. $C_{13}H_9O_2N_3ClI$ requires N, 10·5%), and the *oxime* colourless needles, m. p. 129°, from alcohol (Found : N, 5·3. C_7H_5ONClI requires N, 5·0%).

3-*Chloro*-4-*iodobenzoic acid* crystallises from glacial acetic acid in colourless plates, m. p. 219° (0·1412 g.; 0·1862 g.; 0·1892 g.).

3-*Bromo*-4-*iodobenzaldehyde* crystallises from alcohol in colourless needles, m. p. 66° (0·1550 g.; 0·2140 g.; 0·2115 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 260—261° (decomp.), from dilute alcohol (Found: N, 9·6. $C_{13}H_9O_2N_3BrI$ requires N, 9·4%), and the *oxime* colourless needles, m. p. 157—158°, from alcohol (Found: N, 4·5. C_7H_5ONBrI requires N, 4·3%).

3-*Bromo*-4-*iodobenzoic acid* crystallises from glacial acetic acid in colourless plates, m. p. 242—243° (0·1630 g.; 0·2062 g.; 0·2115 g.).

3 : 4-*Di-iodobenzaldehyde* crystallises from alcohol in colourless, micro-crystalline needles, m. p. 118° (Found: I, 71·0. $C_7H_4OI_2$ requires I, 70·95%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 245—247° (decomp.), from dilute alcohol (Found: I, 51·3. $C_{13}H_9O_2N_3I_2$ requires I, 51·6%), and the *oxime* colourless needles, m. p. 177—178°, from alcohol (Found : I, 68·2. $C_7H_5ONI_2$ requires I, 68·1%).

3 : 4-Di-iodobenzoic acid crystallises from glacial acetic acid in colourless plates, m. p. 256—258° (Wheeler and Liddle, *Amer. Chem. J.*, 1909, 42, 444, give m. p. 257°) (Found : I, 67·7. Calc.: I, 67·9%).

The authors desire to thank the Department of Scientific and Industrial Research for a grant to one of them (H. G. B.), and Messrs. J. W. Leitch and Co. and the British Dyestuffs Corporation for gifts of chemicals.

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IV.—*Arylseleninic Acids.*

By WILLIAM HENRY PORRITT.

Two tolueneseleninic acids have been recorded by Doughty and Elder (Eighth Inter. Congress Applied Chemistry, 1912, 6, 93) as resulting from the reduction by hydrochloric acid of the mixed tolueneselenonic acids obtained by the direct action of selenic acid on toluene. The *p*-substituted acid was described as containing $1H_2O$ and melting with decomposition at 160°, whereas the *o*-isomeride, with melting point 99—101°, was stated to contain $\frac{1}{2}H_2O$.

The *m*-seleninic acid and two xyleneseleninic acids not hitherto described and the foregoing *o*- and *p*-tolueneseleninic acids have now been obtained from definitely oriented aromatic derivatives.

A correction. The action of hydrogen peroxide on two arylselenoglycollic acids was stated by Morgan and Porritt (J., 1925, **127**, 1758) to give rise to the corresponding arylselenoxyglycollic acids. Mr. F. C. Ray, of Battersea Polytechnic, kindly notified the author that this statement is erroneous, and further investigation has shown that the oxidising action of the hydrogen peroxide is sufficiently violent to remove the $CH_2\cdot CO_2H$ group and give the corresponding arylseleninic acids.

This oxidation process, which has been repeated and extended, affords a ready and general method for preparing arylseleninic acids containing substituents of known orientation. If the temperature is allowed to rise appreciably during the first stage of the reaction between hydrogen peroxide and the arylselenoglycollic acid, the formation of the arylseleninic acid is attended by the production of other oxidation products and diaryl diselenides also may be isolated. The tolueneseleninic acids as prepared by this general method are obtained in anhydrous forms.

EXPERIMENTAL.

o-*Tolylselenoglycollic acid*, $CH_3\cdot C_6H_4\cdot Se\cdot CH_2\cdot CO_2H$, was prepared by the general method (Morgan and Porritt, *loc. cit.*, p. 1775) from magnesium *o*-tolyl bromide and selenium (Taboury, *Bull. Soc. chim.*, 1903, **29**, 761), the condensation of the potassium salt of the mercaptan with sodium chloroacetate being effected in aqueous solution. The *selenoglycollic acid* separated as an oil from an acidified solution of its sodium salt and solidified slowly; after repeated crystallisation from boiling water, it was obtained in colourless, lustrous plates, m. p. 70—71° (Found: C, 47·2; H, 4·5. $C_9H_{10}O_2Se$ requires C, 47·2; H, 4·4%). It developed a reddish-brown colour in concentrated sulphuric acid.

m-*Xylyl-4-selenoglycollic Acid*, $(CH_3)_2C_6H_3\cdot Se\cdot CH_2\cdot CO_2H$.—4-Iodo-*m*-xylene, prepared from *m*-4-xylidine, was converted by the general reaction into the *selenoglycollic acid*, which separated as an oil and subsequently crystallised in colourless, lustrous plates, m. p. 90·5° (Found: C, 49·5; H, 5·0. $C_{10}H_{12}O_2Se$ requires C, 49·4; H, 4·9%). The acid developed a greenish-yellow colour in sulphuric acid.

o-*Xylyl-4-selenoglycollic acid*, prepared by the general method from 4-iodo-*o*-xylene obtained from *o*-4-xylidine (m. p. 49°; Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, 1926, **45**, 222T), crystallised from hot water in colourless plates, m. p. 88°, and developed a violet coloration in sulphuric acid (Found: C, 49·5; H, 5·1%).

Toluene-o-*seleninic acid*, $CH_3 \cdot C_6H_4 \cdot SeO_2H$, was prepared by adding an excess of 20% hydrogen peroxide to a suspension of *o*-tolylselenoglycollic acid in ice-cold water, the acid gradually dissolving. The product, which separated after several hours, crystallised from hot water in clusters of colourless needles, m. p. 126—127° (Found: C, 41·4; H, 4·0. $C_7H_8O_2Se$ requires C, 41·4; H, 3·9%). It dissolved sparingly in ether and more readily in alcohol or chloroform.

Toluene-p-*seleninic acid*, prepared from *p*-tolylselenoglycollic acid, crystallised from hot water in colourless, flattened needles, m. p. 171° (Found: C, 41·7; H, 4·3%). Like the preceding isomeride, it developed a violet coloration with warm concentrated sulphuric acid and liberated iodine from acidified solutions of potassium iodide.

Toluene-m-*seleninic acid*, prepared by the oxidation with hydrogen peroxide of oily *m*-tolylselenoglycollic acid obtained from 3-iodotoluene through the Taboury reaction, separated from hot water in colourless needles, m. p. 119—120° (Found: C, 41·5; H, 4·0%). It developed a deep blue coloration with warm sulphuric acid.

Bromobenzene-p-*seleninic acid*, $C_6H_4Br \cdot SeO_2H$, prepared from *p*-bromophenylselenoglycollic acid by oxidation with hydrogen peroxide in acetic acid solution, crystallised from hot water in colourless needles, decomp. 187° (Found: C, 27·4; H, 1·9. $C_6H_5O_2BrSe$ requires C, 26·9; H, 1·9%). The sulphuric acid coloration was reddish-purple.

m-*Xylene-4-seleninic acid*, $(CH_3)_2C_6H_3 \cdot SeO_2H$, prepared by the general method of oxidation from the corresponding selenoglycollic acid, crystallised from water in colourless needles, decomp. 146—147° (Found: C, 44·0; H, 4·5. $C_8H_{10}O_2Se$ requires C, 44·2; H, 4·6%).

o-*Xylene-4-seleninic acid* crystallised from hot water in colourless needles, decomp. 125° (Found: C, 44·4; H, 4·7%).

The two xyleneseleninic acids developed deep blue colorations with warm concentrated sulphuric acid.

Di-o-*tolyl selenide*, $Se(C_7H_7)_2$, was prepared by the action of selenium on magnesium *o*-tolyl bromide and isolated during the preparation of *o*-tolylselenoglycollic acid after extraction of the ethereal solution of the selenomagnesium bromide with aqueous caustic potash. By repeated crystallisation from absolute alcohol, it was obtained in flat, colourless, shining plates, m. p. 64° (Found: C, 64·5; H, 5·5. $C_{14}H_{14}Se$ requires C, 64·4; H, 5·4%).

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[*Received, November* 11*th*, 1926.]

V.—*Period of Induction in Chemical Reactions. Interaction of Mercuric Chloride and Sodium Hydrogen Carbonate.*

By PANCHANAN NEOGI and SUKUMAR NEOGI.

WHILST preparing certain compounds of mercury, the authors found that interaction between mercuric chloride and alkaline hydrogen carbonates does not take place at once, but that there is a distinct period of induction. The present paper deals with this particular reaction, and those with other salts are being investigated.

Standard solutions of mercuric chloride and sodium hydrogen carbonate were prepared. 10 C.c. of the sodium hydrogen carbonate solution were added as quickly as possible to 10 c.c. of the mercuric chloride solution in a 50 c.c. test-tube, which was then sharply shaken once; the interval between the moment of mixing and the first appearance of the red precipitate of oxychloride at the top of the mixture was read from a stop-watch. The moment when the last portion of the sodium hydrogen carbonate solution had been poured was taken as the moment of mixing. A lens was used to ascertain the moment when the precipitate first made its appearance at the lowest point of the meniscus, and a black background facilitated the observation. The concentrations of the reactants were varied severally and jointly, giving three sets of experiments: (1) constant concentration of mercuric chloride (Table I); (2) constant concentration of sodium hydrogen carbonate (Table II); and (3) variable concentrations of both mercuric chloride and sodium hydrogen carbonate (Tables III and IV).

The determination of the exact time when the precipitate just became detached from the lowest point of the meniscus required practice and sometimes six determinations were made with one particular mixture, the mean being taken.

TABLE I.

$C_{Hg} = 1·467$; temp. 23°.

C_{Na}.	t.	$C_{Na} \times t = K$.
2·0000	31·5	63·00
1·6666	39·5	65·80
1·4228	45·5	64·97
1·2500	50·5	63·12
1·1110	55·5	61·60
1·0000	65·0	65·00
0·9090	72·0	65·44
0·8334	81·0	67·50
0·7692	85·0	65·38
0·7142	92·0	65·70
	Mean	64·76

TABLE II.

$C_{Na} = 1·723$; temp. 23°.

C_{Hg}.	t.	$C_{Hg} \times t = K$.
1·476	41	60·51
1·2295	48	59·01
1·0548	58	61·17
0·9225	69	60·85
0·8144	78	63·95
0·7380	82	60·52
0·6708	87	58·34
0·6150	95	58·42
0·5676	102·5	58·00
0·5271	110·5	58·24
	Mean	59·90

C_{Hg} and C_{Na} represent concentrations of mercuric chloride and sodium hydrogen carbonate, respectively, in g.-mols. per 10 litres of water (10 c.c. of each solution were used in each experiment); t is the period of induction in seconds.

For the experiments in Tables III and IV, each reactant was diluted to 0·835, 0·71, 0·625, 0·55, 0·50, 0·45, 0·42, 0·38, and 0·36 of its original concentration (see Fig. 1), but the values of C_{Na} in Table IV are double the corresponding values in Table III, the values of C_{Hg} remaining the same.

FIG. 1.

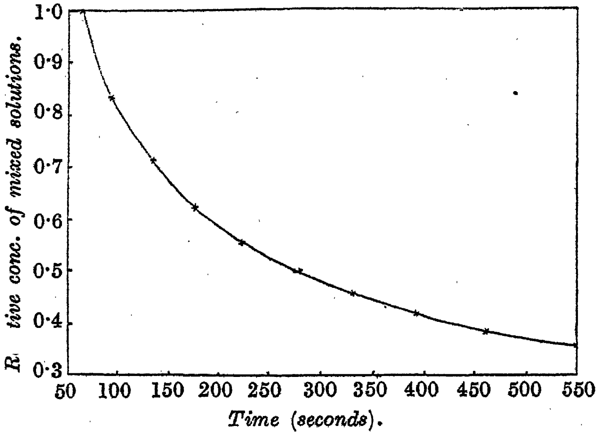


TABLE III.

Temp. 23°.

C_{Hg}.	C_{Na}.	t.	$C_{Na} . C_{Hg} . t = K$.
1·4760	1·000	65	95·94
1·2295	0·833	92	94·22
1·0547	0·7143	133	99·16
0·9225	0·625	175	100·89
0·8199	0·5555	221	100·65
0·7380	0·5000	270	99·63
0·6708	0·4545	330	104·61
0·6150	0·4167	392	104·69
0·5676	0·3846	460	100·43
0·5271	0·3571	550	103·52
			Mean 100·37

TABLE IV.

Temp. 23°.

C_{Na}.	t.	$C_{Na} . C_{Hg} . t = K$.
2·000	32	95·46
1·666	46	94·22
1·428	68	102·42
1·250	90	103·78
1·111	112	102·02
1·000	130	95·94
0·909	154	93·90
0·8334	190	97·49
0·7692	225	98·24
0·7143	250	96·63
		Mean 98·01

From Tables I—IV it will be seen that the period of induction is approximately inversely proportional to the concentration of the solutions. It was not possible to get more concordant results, as the reaction is apparently very complex (*vide infra*).

Effect of Temperature.

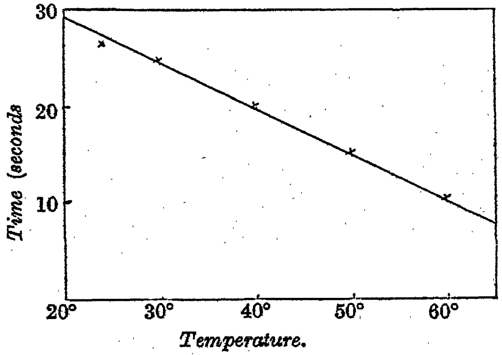
The two solutions contained in large test-tubes were kept in a glass thermostat for ½ hour, then the sodium hydrogen carbonate was immediately poured into the test-tube containing the mercuric chloride, and the period of induction read from the stop-watch. The experiment was repeated at 24°, 30°, 40°, 50°, and 60°, the concentrations of mercuric chloride and sodium hydrogen carbonate being kept constant. 10 C.c. of mercuric chloride ($C_{Hg} = 1{\cdot}476$) and 10 c.c. of sodium hydrogen carbonate ($C_{Na} = 2{\cdot}000$) were taken in each experiment.

TABLE V.

Temperature	24°	30°	40°	50°	60°
Period of induction (secs.) ...	31·5	26·1	20·0	15·0	10·5

The period of induction therefore diminishes, as the temperature is increased, approximately at the rate of 5 secs. for every increase of 10° (see Fig. 2).

FIG. 2.



The possible conversion of sodium hydrogen carbonate into carbonate when the temperature was raised was also studied; in addition to the two test-tubes containing mercuric chloride and sodium hydrogen carbonate, a third test-tube containing 10 c.c. of the same sodium hydrogen carbonate solution was suspended for ½ hour in the thermostat in each experiment under the same conditions of temperature. The conversion of hydrogen carbonate into carbonate was estimated with standard sulphuric acid solution by the double-indicator method:

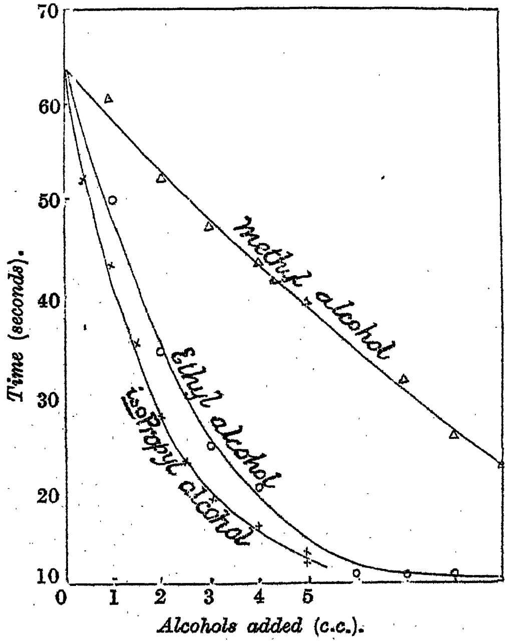
Temperature	30°	40°	50°	60°
Carbonate formed ...	0·000598	0·000653	0·000761	0·010332

The proportion of carbonate in the hydrogen carbonate increases with the rise of temperature from 30° to 60°. Sodium hydrogen carbonate solution (1 : 14) was found not to change during 24 hours at laboratory temperature.

Effect of Light.

Solutions of mercuric chloride ($C_{\mathrm{Hg}} = 1{\cdot}476$) and sodium hydrogen carbonate ($C_{\mathrm{Na}} = 2{\cdot}00$) were prepared in the dark-room and kept over-night. The period of induction, noted in red light on the following day, was found, after some trials in order to adjust vision in red light, to be the same as that in diffused daylight, *viz.*, 32 secs. at 22°. The reaction is therefore not photochemical.

FIG. 3.



Action of Alcohols.

The effect of alcohols and sugars on the period of induction was next studied. Methyl and ethyl alcohols progressively diminished the period of induction up to a certain limit. *iso*Propyl alcohol accelerated the reaction and hence diminished the period of induction, whereas *n*-propyl alcohol increased the period of induction so greatly that with 1·5 c.c. added to 20 c.c. of the mixture no precipitate was observed within ½ hour. In fact, *n*- and *iso*-propyl alcohols may be distinguished with the help of a dilute solution of mercuric chloride and sodium hydrogen carbonate. Glycerol caused a pronounced increase in the period of induction, but glucose, sucrose, mannitol, and dulcitol had very little effect.

The concentrations of the two solutions were kept constant ($C_{\mathrm{Hg}} = 1\cdot457$; $C_{\mathrm{Na}} = 1\cdot000$); 10 c.c. of each solution were taken each time and the amount of alcohol added was increased, the alcohol being mixed with the mercuric chloride solution and the whole being cooled to 22° before the sodium hydrogen carbonate solution was added. The effects of methyl, ethyl, and *iso*propyl alcohols are plotted in Fig. 3.

Methyl alcohol (c.c.)	0	1	2	3	4	5	6	7	8	9	10
t (secs.)	67	62	52	47	43	39	37	31	25	22	20
Ethyl alcohol (c.c.)	0	1	2	3	4	5	6	7	8	9	
t (secs.)	63	50	34	24	20	15	12	11	11	11	
n-Propyl alcohol (c.c.)	0	0·2	0·4	0·6	0·8	1·0	1·5	2·0			
t (secs.)	63	108	132	143	160	1100	1200	1500			
*iso*Propyl alcohol (c.c.)	0	0·5	1·0	1·5	2·0	2·5	3·0	4·0	5·0		
t (secs.)	63	52	43	35	27·5	22·5	19	16	14		

Glycerol (c.c.)	0	1	2	3
t (secs.)	63	129	165	221

Wt. of substance added.	*t* (secs.).	Wt. of substance added.	*t* (secs.).
nil.	73*	0·0884 g. mannitol	74
0·4309 g. glucose	75	0·1235 „ „	75
0·2345 „ „	74	0·0775 „ dulcitol	75
0·2034 „ sucrose	74	0·0926 „ „	75·5
0·1245 „ „	74		

* This mixture was not of the same concentration as the foregoing.

Salts.

For obvious reasons, the effects of acids and alkalis could not be studied, but the action of certain salts, inorganic and organic, was investigated. 5 C.c. of an $M/10$-solution of a salt and 10 c.c. each of mercuric chloride and sodium hydrogen carbonate solutions were taken in each experiment, the temperature being 25°.

TABLE VI.

Substances added.	*t* (secs.).	Substances added.	*t* (secs.).
Water (5 c.c.)	28	Na Citrate	49
NaCl	68	K Citrate	48
KCl	67	Na Oxalate	54
Na_2SO_4	27	K Oxalate	54
K_2SO_4	27	$NaNO_3$	29
Na Tartrate	24	KNO_3	29
K Tartrate	24		

Table VI shows that chlorides, citrates, and oxalates markedly lengthen the period of induction, tartrates diminish it, and sulphates and nitrates have scarcely any action; *further, that anions, but not* cations, influence the period of induction. This is quite in conformity with the work of Berczeller (*Int. Z. Biol.*, 1916, **2**, 444), who has shown that the effects of salts on the period of induction in the interaction of iodic and sulphurous acids are also dependent on the anions and not on the cations.

Discussion of Results.

The results given above establish the following points :

1. The period of induction is inversely proportional to the concentrations of each reactant, temperature being constant.
2. It diminishes with rise of temperature.
3. It increases with the addition of *n*-propyl alcohol, glycerol, chlorides, oxalates, and citrates, and diminishes with the addition of tartrates and of methyl, ethyl, and *iso*propyl alcohols. Nitrates, glucose, sucrose, mannitol, and dulcitol have no effect on the period of induction.

The present work agrees with Landolt's work on the action of sulphurous and iodic acids (*Ber.*, 1886, **19**, 1317) in that the period of induction in both cases is inversely proportional to the concentrations of the reactants.

The problem now is to determine the reactions which cause this period of induction. In the reaction between iodic and sulphurous acids, the separation of iodine is supposed to take place in several stages through iodous, hypoiodous, and hydriodic acids. In the case of mercuric chloride and sodium hydrogen carbonate, the intermediate reactions are obscure and complex. Under the conditions of our experiments, a red precipitate of the constitution $HgCl_2,2HgO$ is formed along with small quantities of the yellow oxychloride $HgCl_2,3HgO$. The black variety, $HgCl_2,2HgO$, is not formed until the red precipitate has been kept for some days. The formation of these oxychlorides has been reported by many workers, *e.g.*, Biltz (*Arch. Pharm.*, 1869, **190**, 202) and Thummel (*ibid.*, 1889, **27**, 589). It is evident that no carbonate is precipitated, and that carbon dioxide is evolved. Biltz thought that excess of sodium hydrogen carbonate formed a double salt, but Thummel has shown that the precipitate does not contain any mercuric carbonate, carbon dioxide being given off. We are of the opinion that the *formation of the oxychloride by the action of alkali hydrogen carbonate on mercuric chloride can never be instantaneous*. It would be more reasonable to suppose that mercuric carbonate or hydrogen carbonate is first formed and then combines with mercuric chloride in stages with the formation of oxychlorides and liberation of carbon dioxide. The work of previous workers shows that the two oxychlorides, $HgCl_2,2HgO$ (red) and $HgCl_2,3HgO$ (yellow), are precipitated; whilst the unstable $2HgCl_2,HgO$ and $HgCl_2,HgO$ are probably formed as intermediate compounds, *e.g.*:

$$Hg(HCO_3)_2 + 2HgCl_2 = 2HgCl_2,HgO \text{ (unstable)} + 2CO_2 + H_2O;$$
$$2HgCl_2,HgO + Hg(HCO_3)_2 = 2HgCl_2,2HgO \text{ (unstable)} + 2CO_2 + H_2O.$$

Since the velocity of a reaction is proportional to the amount of the reacting substances, the speed of the formation of the red oxychloride is the result of the velocities of successive reactions such as those above, and the belated appearance of the red precipitate—the period of induction—corresponds with the time required for the consecutive reactions to take place before the actual precipitation of the red compound could commence. The fact that mercuric chloride is very feebly ionised in aqueous solution accounts for the smallness of the precipitate. That it has material influence on the period of induction also will be apparent from the following considerations:

(*a*) The slight ionisation of mercuric chloride in aqueous solution does not greatly increase with further dilution, and the number of ions present in solutions in which the concentration of mercuric chloride gradually diminishes therefore becomes less and less. As the velocity of ionic reactions depends on the concentration of the ions, it is evident that with further dilution the velocities of the intermediate reactions would be retarded, and hence the period of induction would increase.

(*b*) Arrhenius and others have shown that the ionisation of mercuric chloride increases in the presence of alcohols. This would explain the relatively large precipitate with alcoholic solutions of mercuric chloride and also the decrease in the period of induction in the case of methyl and ethyl alcohols, for, with increased ionisation, the velocities of the intermediate reactions would increase and hence the period of induction would decrease.

(*c*) Since rise of temperature also increases ionisation, the period of induction would decrease owing to the increased velocities of the intermediate reactions.

The action of methyl, ethyl, and *iso*propyl alcohols in shortening the period of induction may also be due to catalytic action. Their presence hastens the rates of the intermediate reactions, for it has been shown by Thummel (*Arch. Pharm.*, 1889), **27**, 589 that alcohols readily decompose the oxydichloride to the red dioxychloride. The catalytic effect of the alcohols in this case increases with their concentrations to a certain limit. Sodium chloride inhibits the reactions owing to the formation of double salts with mercuric chloride. The action of glycerol, nitrates, citrates, tartrates, and oxalates is probably catalytic in nature.

Conclusions.

1. A distinct period of induction precedes the precipitation of the red oxychloride in the interaction between mercuric chloride and sodium hydrogen carbonate.

2 The period of induction is inversely proportional to the concentration of each reactant, the temperature of the system being constant.

3. It diminishes as the temperature is raised, evidently owing to the increased velocities of intermediate reactions. It diminishes approximately at the rate of 5 seconds for a temperature increase of 10°.

4. The period of induction is the result of several successive reactions which take place before the final appearance of the red dioxychloride of mercury.

5. It diminishes with the addition of methyl, ethyl, or *iso*propyl alcohol or of tartrates, and increases with the addition of glycerol, *n*-propyl alcohol, chlorides, citrates, and oxalates. Sugars, such as glucose and sucrose, and polyhydric alcohols, such as mannitol and dulcitol, as well as nitrates and sulphates have scarcely any effect on the period of induction. The period of induction is influenced by the anions of salts and not by the cations.

6. The reaction is not photochemical in nature.

7. The feeble ionisation of mercuric chloride in aqueous solution explains the small quantity of precipitate produced. It has material influence on the period of induction also, since, owing to the low concentrations of ions on further dilution, the velocities of the intermediate reactions would be lessened and therefore the period of induction would increase. The reverse result is obtained when the ionisation of mercuric chloride is increased by the presence of methyl and ethyl alcohols or by raising the temperature.

8. A very dilute solution of mercuric chloride and sodium hydrogen carbonate may be used to distinguish between *n*- and *iso*-propyl alcohols: with the latter the precipitate of the red oxychloride appears within a few seconds, whilst with the normal alcohol the precipitation takes much longer—even more than ½ hour.

PRESIDENCY COLLEGE, CALCUTTA.

[*Received, May 3rd,* 1926.]

VI.—*The Propagation of Flame in Mixtures of Methane and Air. Part V. The Movement of the Medium in which the Flame Travels.*

By WILLIAM RONALD CHAPMAN and RICHARD VERNON WHEELER.

PART IV of this research (J., 1926, 2139) described the determination of the conditions under which the flame travelling along a tube in a mixture of methane and air, initially quiescent and at atmospheric temperature and pressure, acquired its maximum speed. When the tube was 2—3 m. in length and 5 cm. in diameter, the conditions were that both ends should be open (ignition of the mixture being at one end) and that a number of restricting rings, reducing the diameter of the tube to one-half, should be introduced close together a short distance (50—100 cm.) from the point of ignition. Under these conditions, a speed as high as 420 m./sec. was obtained beyond the restrictions, the highest speed in an unrestricted tube of the same dimensions being about 6 m./sec.

It was shown that, during the propagation of flame in a tube open at both ends, the unburnt mixture in advance of the flame-front travels as a current in the same direction, and the flame is therefore moving in a medium which is itself in motion. The flame-speed at any point in the tube thus depends largely on the speed acquired by the medium, and the effect of restrictions is explained as being mainly an effect on the movement of the medium.

We have continued the study of the propagation of flame under different conditions in tubes restricted at certain points so as to control the movement of the unburnt mixture ahead of the flame. In this manner, we hoped to gain further information regarding the extent to which the movement of the flame depends on that of the medium in which it travels. All the experiments were made with a mixture of methane and air containing 9·5—10·0% of methane, using the brass tube, 5 cm. in diameter and 240 cm. long, previously described. The behaviour of the flame was studied by photographing it through a quartz lens on a rapidly revolving film as it passed a quartz window, 40 cm. long and 4 mm. wide, which could be placed in any desired position along the tube.

We have attempted to explain all the following results on the assumption that, under all conditions, there is a movement of the unburnt mixture ahead of the flame caused by the expansive force of the burning gases.

(A) *Ignition at One End of a Horizontal Tube Open at Both Ends.*

It has been recorded that when the tube is fully open at both ends the speed of the flame increases regularly over the first 80 cm. and is then slightly retarded (undulations making their appearance) to increase again after this temporary check. The initial acceleration of the flame is assumed to be due to the increasing speed with which the unburnt mixture is caused to move under the expansion of the burning gases. The acceleration would no doubt continue regularly throughout the length of a sufficiently short tube, but, in such a long tube as that used, cooling and condensation of the products of combustion cause a fall in pressure behind the flame which reduces the rate of acceleration of the unburnt mixture. As the flame travels further from the open end, the deficiency of pressure due to cooling and condensation being then less readily rectified by communication with the external atmosphere, the unburnt mixture, and therefore the flame, is retarded.

(a) *The Influence of a Restriction at the Ignition End of the Tube.*—The mean speeds of the flame over successive intervals when the end of the tube at which ignition was effected was reduced in diameter to 1·5 cm. are recorded in Table I. The speeds when the tube was fully open at both ends (see Part IV, Table I) are given for comparison. Similar, but less marked, results were obtained when the diameter of the tube at the ignition end was reduced to 2·5 cm.

Fig. 1, Plate I, is a composite photograph,* obtained in the manner described in Part IV, illustrating the manner in which the flame travels in a 9·75% methane–air mixture. This photograph should be compared with Fig. 1, Plate I, of Part IV.

TABLE I.

The Effect of Restricting the Ignition End of a Tube Open at Both Ends.

	Mean speed of flame (cm./sec.).			Mean speed of flame (cm./sec.).	
Distances from point of ignition (cm.).	Tube fully open at both ends.	Diam. at ignition end reduced to 1·5 cm.	Distances from point of ignition (cm.).	Tube fully open at both ends.	Diam. at ignition end reduced to 1·5 cm.
5—15	106	192	85— 95	249	827
15—25	134	220	95—125	229	1034
25—35	152	260	125—135	285	900
35—65	194	412	135—145	350	791
65—75	240	618	145—175	441	1016
75—85	254	721	175—205	575	1800

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* This photograph is reduced to about ⅛th of the size of the original; allowing for this, the speed of travel of the film can be regarded as 11·5 cm./sec.

The partial closure of the ignition end impedes the release of pressure at that end, so that a greater and more prolonged pressure is available to propel the column of unburnt mixture ahead of the flame. The speed of the flame is thus more rapidly accelerated than when the ignition end of the tube is fully open, and a further distance is travelled (125 cm. as compared with 80 cm.) before the influence of cooling behind the flame causes a retardation. This retardation is, however, greater in the former case, there being a 25% as compared with a 10% reduction in speed, because communication with the outside air is restricted.

(b) *The Influence of a Restriction at the Ignition End of the Tube together with Restrictions in the Path of the Flame.*—When the end of the tube at which the mixture was ignited was partly closed and one or more restricting rings were introduced at intervals along the tube, the speed of the flame during its passage depended upon the amount of restriction at each point, except that reduction of the diameter of the tube at the ignition end to 1·5 cm. or less was no more effective than reduction to 2·5 cm. Indeed, when there were two or three restrictions in the tube, the maximum effect on the speed of the flame was obtained when the diameter at the ignition end was 2·5 cm., whilst, as recorded in Part IV, when there were several restrictions close together, the maximum effect was obtained with both ends of the tube fully open.

The mean speeds of the flame before and after passing one restricting ring, 110 cm. from the ignition end of the tube, the diameter of which was reduced to 2·5 cm., are recorded in Table II.

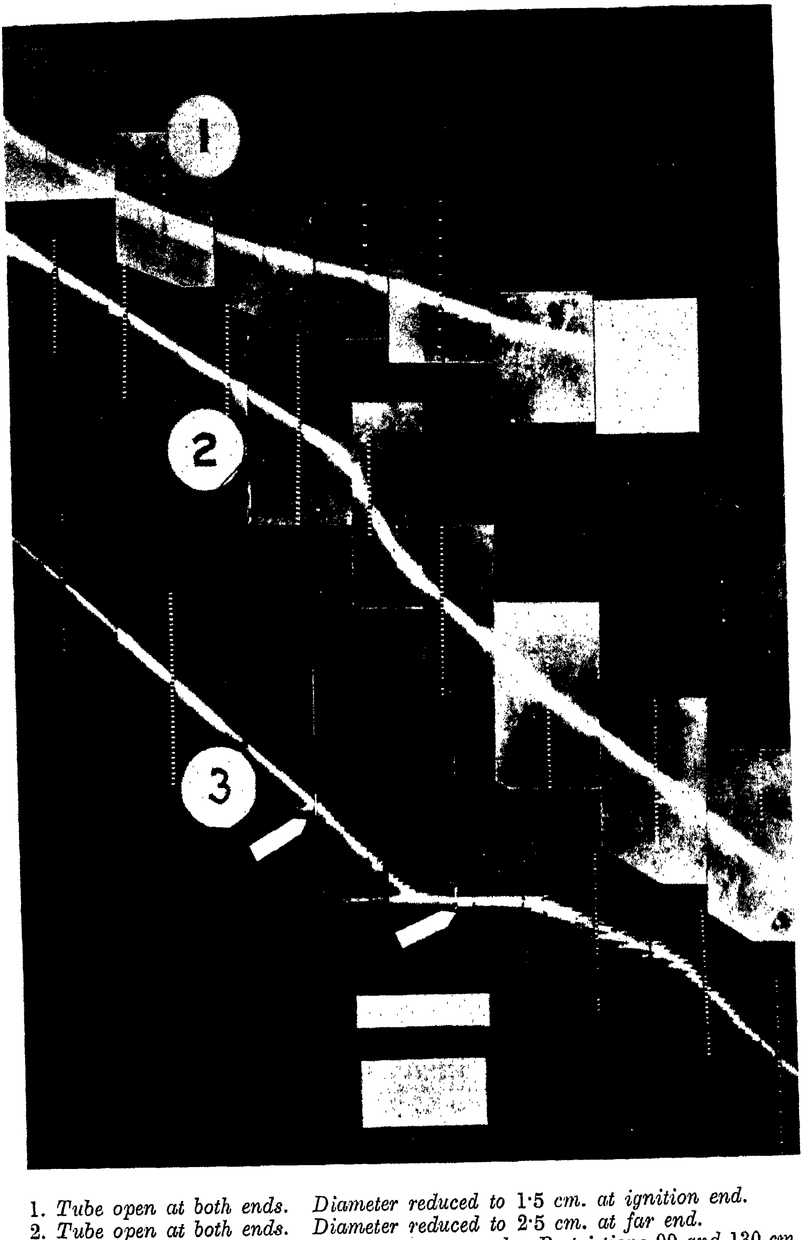
TABLE II.

The Effect of One Restriction in a Tube with Restricted Ignition End.

	Mean speed of flame (cm./sec.).	
Distance from point of ignition (cm.).	Aperture in restriction 2·5 cm. diam.	Aperture in restriction 1·0 cm. diam.
75— 85	256	95
85— 95	289	84
95—105	307	83
105—115	Restriction at 110.	Restriction at 110.
115—125	1860	2200
125—135	1882	3666
135—145	1766	5,077
145—155	1527	6,455
155—165	1319	7,833
165—175	1424	10,070
175—185	1458	14,100

The movement of the mixture away from the point of ignition is checked by the restriction at 110 cm., the more so the narrower the passage, and the speed of the flame is therefore slow. When the flame has passed the restriction, however, there is no resistance

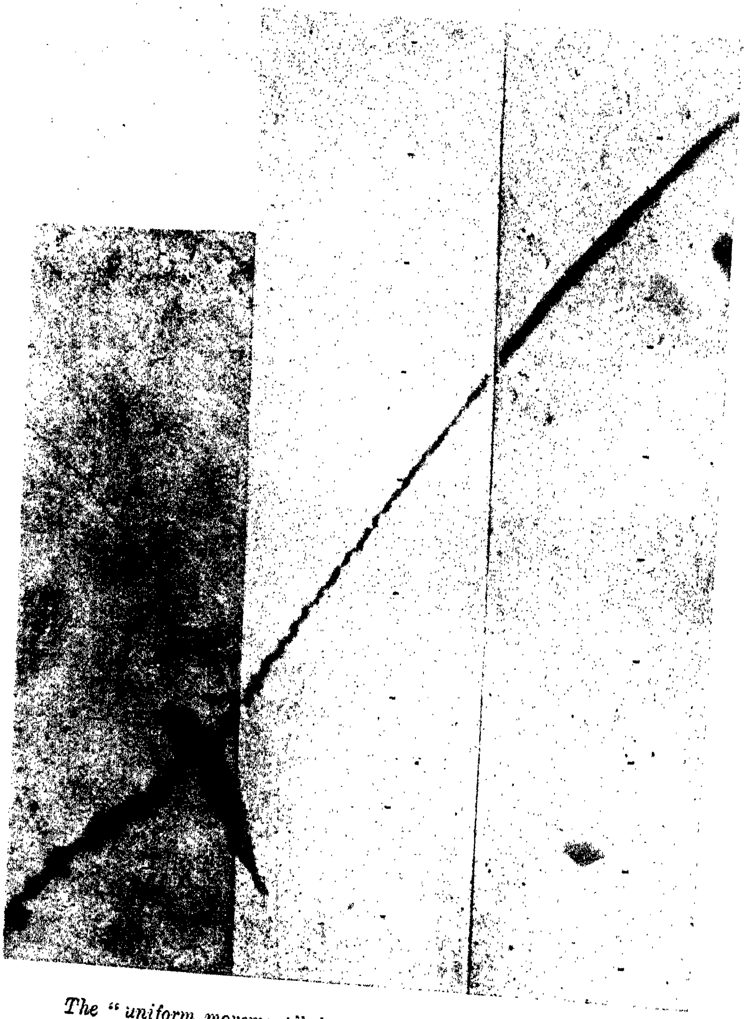
PLATE I.



1. *Tube open at both ends. Diameter reduced to* 1·5 *cm. at ignition end.*
2. *Tube open at both ends. Diameter reduced to* 2·5 *cm. at far end.*
3. *Tube closed at one end. Ignition at open end. Restrictions* 90 *and* 130 *cm. from open end.*

[*To face p.* 40.]

PLATE II.



The "uniform movement" in a 30·9% hydrogen-air mixture.

(other than frictional) to the passage of the mixture along the tube, whilst release of pressure towards the ignition end of the tube is impeded, in proportion as the aperture of the restricting ring is smaller. The speed of movement of the mixture, and thus of the flame which travels in it, therefore rapidly increases.

Table III.

(In sections A, B, C, and D the mean speed of flame is that measured over a distance of 30 cm. immediately beyond the last restriction.)

(A) *Diameter at ignition end reduced. Two restrictions, apertures each* 1 *cm. in diameter,* 90 *and* 130 *cm. respectively from ignition end.*

Diam. at ignition end (cm.).	2·5	1·5	1·0
Mean speed of flame (m./sec.).	131·3	58·7	Flame extinguished.

(B) *Diameter at ignition end reduced to* 2·5 *cm. One restriction* 110 *cm. from ignition end.*

Diam. of aperture of restriction (cm.).	2·5	2·0	1·5	1·0	0·5
Mean speed of flame (m./sec.).	17·3	27·0	28·7	30·1	46·0

(C) *Diameter at ignition end reduced to* 2·5 *cm. Two restrictions, apertures each* 1 *cm. in diameter, at different distances from ignition end.*

Positions of restrictions, measured from ignition end (cm.).	(i)	20	40	60	40	60	50	60	60	90	120	150
	(ii)	80	80	80	110	110	90	90	110	130	150	180
Mean speed of flame (m./sec.).		48·2	83·3	66·7	89·5	67·8	92·9	164·5	86·5	131·5	84·6	53·4

(D) *Diameter at ignition end reduced to* 2·5 *cm. Three restrictions, with apertures of different diameters, at different distances from ignition end.*

Diam. of aperture of restriction (cm.).	(i)	2·0	2·0	2·0	2·0	2·0
	(ii)	1·5	1·5	1·5	1·5	1·0
	(iii)	0·5	1·0	1·0	1·0	1·5
Positions of restrictions, measured from ignition end (cm.).	(i)	60	60	40	20	20
	(ii)	90	90	70	50	50
	(iii)	130	130	110	90	90
Mean speed of flame (m./sec.).		Flame extinguished.	60·9	100·9	75·0	83·8

(E) *Diameter at ignition end reduced to* 2·5 *cm. Two restrictions, with apertures of different diameters,* 90 *and* 130 *cm., respectively, from ignition end. (Mean speeds of flame between the restrictions, in cm./sec.)*

Distance from point of ignition (cm.).	95—105	105—115	115—125
Apertures 1·0 cm. diam.	1247	796	388
Apertures 1·5 cm. diam.	1182	732	461
Apertures 2·0 cm. diam.	866	709	600

When two restricting rings were present, each with apertures of 1 cm. and placed 40 cm. apart, the highest speed of flame, measured over a distance of 30 cm. just beyond the second restriction, was obtained when the ignition end of the tube was reduced in diameter to 2·5 cm., the mean value being 130 m./sec. as compared with 58·7 m./sec. when the diameter at the ignition end was 1·5 cm. Increasing the number of restrictions to three or more, the ignition end being 2·5 cm. in diameter, did not always result in an enhanced speed of flame. If the diameter of the apertures was only 1 cm., a greater number of restrictions than two decreased the speed attainable by the flame, or sometimes caused its extinction. When their aperture was 2·5 cm., three and four restrictions enabled speeds of flame of 310 and 390 m./sec., respectively, to be attained, the removal of the restriction at the ignition end reducing these velocities to 225 and 280 m./sec., respectively.

The results of typical experiments with a number of different arrangements of the restricting rings, made in an endeavour to develop the fastest flames, are given in Table III.

Beyond the first of two restrictions, the flame moves more rapidly the greater the reduction in diameter of the tube, for the reason given when considering the effect of one restriction, but the second restriction impedes the movement of the current of mixture ahead of the flame, and hence the speed is not so great as in its absence (compare Table II). The resistance offered by the second restriction is greater the smaller the aperture, so that the speed of the current, and of the flame, as it approaches the second restriction is lowest when the aperture is smallest.

(c) *The Influence of a Restriction at the Far End of the Tube.*—The result of reducing to 2·5 cm. the diameter of the end of the tube towards which the flame travelled, the ignition end remaining fully open, is recorded in Table IV.

TABLE IV.

The Effect of Restricting the Far End of a Tube Open at Both Ends.

Distance from point of ignition (cm.).	Mean speed of flame (cm./sec.).	
	Tube fully open at both ends.	Diam. at far end reduced to 2·5 cm.
5—15	106	98
15—25	134	110
25—35	152	117
35—65	194	122
65—75	240	125
75—85	254	127
85— 95	249	—
95—125	229	63
125—135	285	—
135—145	350	90
145—175	441	91
175—205	575	93

A composite photograph recording the progress of the flame throughout the length of the tube is shown in Fig. 2, Plate I. The speed of travel of the film in this photograph can be regarded as 3·5 cm./sec.

The comparatively slow speed of the flame throughout the tube can be attributed to the resistance offered by the restriction to the movement of the current of unburnt mixture ahead of the flame, the conditions approximating to those obtaining with a longer tube. In this connexion, the experiments of Mason and Wheeler (J., 1920, **117**, 36) with a tube 30·5 cm. in diameter may be recalled. When this tube, fully open at both ends, was 15·25 m. long, the flame in a 9·5% methane–air mixture travelled from end to end with increasing speed; but when the length was increased to 90 m., the general behaviour of the flame was as though the far end of the tube were closed, its velocity over the first 12—15 m. being slow and nearly uniform.

(B) *Ignition at the Open End of a Horizontal Tube Closed at the Other End.*

In an unrestricted tube, closed at one end, ignition of an inflammable mixture at the open end leads to the " uniform movement " of flame, which persists over about one-third of the length of the tube. When a restriction is introduced at some point along the tube, the movement of the flame is disturbed locally, its rate being reduced before the restriction is reached and increased over a short distance beyond it. Thus the speed of the uniform movement in a 10% methane–air mixture in the unrestricted tube was about 90 cm./sec., whereas when two restrictions were introduced reducing the diameter to 3·2 and 2·5 cm., respectively, at points 90 and 130 cm. from the open end, the velocity fell to 80 cm./sec. An acceleration occurred beyond each restriction. These effects are illustrated by Fig. 3, Plate I.* There can be no extensive movement of the mixture from an open to a closed end of a tube. The speed of the flame is therefore comparatively slow and is not greatly affected by the introduction of an impediment to movement of the mixture. The propagation of flame during the " uniform movement " is discussed later.

(C) *Ignition at the Closed End of a Horizontal Tube Open at the Other End.*

In short, wide, unrestricted tubes the fastest flame in any mixture of methane and air is normally obtained when the mixture is ignited at the closed end of a tube which is open at the other end. For long tubes, however, the flame becomes vibratory and does not reach the open end, because cooling of the products of combustion periodically causes a backward movement of the unburnt mixture and of the flame, with the eventual extinction of the latter by the burnt gases.

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* The speed of travel of the film in this photograph can be regarded as 3·0 cm./sec.

In the comparatively short tube used in these experiments, the flame was extinguished by a restriction unless this was placed fairly close to the point of ignition and its aperture was of not less than 2·5 cm. diameter. Even if these conditions were fulfilled, the introduction of a second restriction resulted in the extinction of the flame at the latter; when both apertures were 2·5 cm. in diameter and they were 80 and 120 cm. from the closed end, the mean speed of the flame increased from 26·2 to 77·5 m./sec. on passing the first restriction, whilst a retrograde secondary flame was set up at this point, as in the case of the tube open at both ends.

(D) *The "Uniform Movement" of Flame.*

We have pointed out that when a flame is travelling from an open towards a closed end of a tube there cannot, at the outset, be any extensive movement of the unburnt mixture ahead of the flame, and that the comparatively slow speed of the flame is thus explicable. Nevertheless, some movement must take place (although we have been unable to detect any current with certainty by direct measurement during the propagation of flame) and, if the assumption be correct that the speed of propagation of flame is affected under all conditions by the movement of the medium in which it travels, it is not to be expected that there should be a strictly "uniform movement" of flame over one-third the length of the tube. Rather would one expect an initial acceleration, slight but appreciable, followed by an equally slight retardation.

With a view to detect slight departures from strict uniformity of movement, we photographed the flame travelling in a 9·75% methane–air mixture over the first 80 cm. of the tube, on a film revolving at such a rate that slight differences in the velocity of the flame could readily be measured. The results are recorded in Table V.

TABLE V.

The Uniform Movement of Flame in a 9·75% Methane–Air Mixture.

Distance along tube (cm.).	0—10	10—20	20—30	30—40	40—50	50—60	60—70	70—80
Speed of flame (cm./sec.).	87·7	89·45	91·5	92·5	91·75	91·2	90·8	90·55

Although the speed of the flame is nearly uniform, there are just such slight variations as would be anticipated if some motion, affecting the speed of the flame, were imparted to the mixture. In conformity with the general argument now advanced, the implication is that the speed of the uniform movement of flame is compounded of (1) the normal rate of propagation of flame by conduction of heat, and (2) the initial motion of the unburnt mixture towards the closed end of the tube. The speed of the latter should increase with increase in the diameter of the tube. There should therefore be a definite relationship between the speed of "uniform movement" of flame in a given mixture and the diameter of the tube in which it travels.

Such determinations for mixtures of 10% of methane in air were made by Mason and Wheeler (J., 1917, **111**, 1044) for the last five tubes shown in Table VI and by Payman and Wheeler (J., 1918, **113**, 656) for the smaller tubes.

TABLE VI.

The Uniform Movement of Flame in Tubes of Different Diameters. 10% Methane–Air Mixture.

Diam. of tube (cm.).	0·45	0·56	0·72	0·81	0·90	2·5	5·0	9·0	30·5	96·5
Speed of uniform movement (cm./sec.).	33·5	41·2	46·3	47·4	48·0	66	92	104	168	250

On plotting the logarithm of the diameter of the tube against that of the flame-speed, the points are found to lie on a straight line. There appears, therefore (for the range of diameters considered), to be a relationship between the speed of the uniform movement of flame, V, and the diameter, D, of the tube in which it travels, of the form $V = cD^k$, k and c being constants.

Mason and Wheeler, in their discussion of the cause of variation of the speed of the uniform movement with the diameter of the tube (*loc. cit.*, p. 1052), assumed that when the diameter exceeds 10 cm. the speed is affected by the coming into play of heat transference by convection. It is clear from the relationship now given, whatever may be its full meaning, that such an assumption is unnecessary, and that no new factor affecting the propagation of flame is introduced after a certain diameter of tube is exceeded. Further, if it be correct to regard this relationship as indicating the effect of increased diameter on the speed of movement of the medium in which the flame travels, a satisfactory explanation, hitherto lacking, is available for the increased speed observed with increased diameter of tube when the flame is propagated downwards from an open towards a closed end (J., 1920, **117**, 1227)—

conditions which should render the effects of heat transference by convection negligible.

Although this communication is directly concerned only with the propagation of flame in mixtures of methane and air, it is not out of place to refer to recent experiments in which Miss E. H. M. Georgeson and Mr. F. J. Hartwell, by photographic analysis, determined the speed of the "uniform movement" in mixtures of hydrogen and air, for they have a direct bearing on the suggestion that the mixture in which the flame is moving is itself in motion. The results are of particular interest to us since they exhibit the initial acceleration of speed, followed by a retardation, which we anticipated; presumably because of the lesser density of the medium in which the flame is travelling, these phenomena are more marked than with mixtures of methane and air (see Table V). We are indebted to Miss Georgeson and Mr. Hartwell for the composite photograph reproduced as Plate II (about $\frac{1}{3}$ its original size), which illustrates admirably the changes of speed during the "uniform movement" of flame in a 30·9% hydrogen–air mixture. The mixture was contained in a horizontal tube of fused silica, 2·5 cm. in diameter, and the flame was photographed through a quartz lens on Lumière paper attached to a drum revolving at such a high speed as to render accurate analysis of the rapid movement possible. The flame is shown travelling from right to left over the first 78 cm. The time-intervals recorded are 0·02 of a second.

We are indebted also to Professor Statham, of this University, who has made a particular study of the problems of mine ventilation, for experimental evidence that in a tube open at one end and closed at the other an appreciable movement of a column of air takes place towards the closed end if a small pressure difference is created at the open end.

These experiments form part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permitting publication.

Department of Fuel Technology,
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[*Received, September 27th*, 1926.]

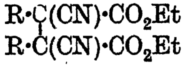
VII.—*The Oxidation of Nitrophenylcyanoacetates.*

By Arthur Fairbourne and Harold Richard Fawson.

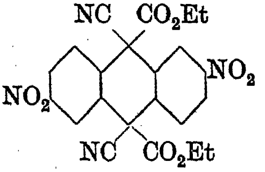
During an investigation on possible methods of synthesising substituted anthracenes (J., 1921, **119**, 1573; 1923, **123**, 1137), certain nitrophenylcyanoacetates were prepared and their hydrolytic and oxidation products examined. Ethyl sodiocyanoacetate was condensed with picryl chloride, 2 : 4-dinitrochlorobenzene and *p*-nitrochlorobenzene, producing ethyl 2 : 4 : 6-trinitrophenylcyanoacetate, ethyl 2 : 4-dinitrophenylcyanoacetate and ethyl *p*-nitrophenylcyanoacetate, respectively.

On oxidation, these nitrophenyl derivatives of ethyl cyanoacetate should produce first the hydroxy-esters, $R\cdot C(OH)(CN)\cdot CO_2Et$ (Meyer, *Ber.*, 1878, **11**, 1283; 1879, **12**, 2238), which would then be capable (i) of losing hydrogen cyanide and becoming ketonic esters, $R\cdot CO\cdot CO_2Et$, (ii) of reacting with unoxidised material to yield substituted succinic esters (I), or (iii) of condensing to form substituted anthracenes (II) of a particularly interesting type (compare Barnett, "Anthracene and Anthraquinone," pp. 50, 69).

(I.)



$$\begin{array}{l} R\cdot C(CN)\cdot CO_2Et \\ \quad | \\ R\cdot C(CN)\cdot CO_2Et \end{array}$$



(II.)

Of these possibilities, (i) and (ii) have been realised. Under identical conditions, ethyl *p*-nitrophenylcyanoacetate was oxidised by chromic anhydride to the substituted succinic ester (I; $R = C_6H_4\cdot NO_2$), which was independently synthesised and its constitution verified; ethyl 2 : 4-dinitrophenylcyanoacetate gave the ketonic ester, $C_6H_3(NO_2)_2\cdot CO\cdot CO_2Et$; and ethyl 2 : 4-dinitrobromophenylcyanoacetate yielded the intermediate hydroxy-ester, $C_6H_2Br(NO_2)_2\cdot C(CN)(OH)\cdot CO_2Et$.

These nitrophenylcyanoacetates are all colourless or slightly yellow in the solid state and in dry organic solvents, but some of them develop intense colour in the presence of water and all do so when treated with alkalis.

EXPERIMENTAL.

Ethyl 2 : 4-*Dinitrophenylcyanoacetate*, $C_6H_3(NO_2)_2\cdot CH(CN)\cdot CO_2Et$. —To a solution of 2·3 g. of sodium in 40 c.c. of alcohol, 11·3 g. of ethyl cyanoacetate were added, followed by a solution of 10 g. of 2 : 4-dinitrochlorobenzene in 30 c.c. of alcohol. After the resulting red mixture had been refluxed on a water-bath for 4—5 hours, the alcohol was removed, 600 c.c. of water added, and the whole acidified with dilute nitric acid. The brown oil that separated was isolated by means of ether and, after solidifying, crystallised several times from alcohol-ligroin. The *ester* was thus obtained in colourless, crystalline needles, m. p. 66° (yield, 90%) (Found: C, 47·1; H, 3·6; N, 15·1. $C_{11}H_9O_6N_3$ requires C, 47·3; H, 3·2; N, 15·1%).

Its structure was proved by hydrolysis with concentrated hydrochloric acid; the 2 : 4-dinitrophenylacetic acid obtained melted at 179° (decomp.), alone or mixed with an authentic specimen (Radziszewski, *Ber.*, 1869, 2, 210).

The ester gave a red solution in wet alcohol and a purple solution in concentrated sulphuric acid. Its *sodium* derivative was precipitated as a red explosive powder when the ester was treated with the theoretical weight of sodium dissolved in alcohol, and ether added (Found: Na, 7·3. $C_{11}H_8O_6N_3Na$ requires Na, 7·6%). The sodium could not be replaced directly by a radical, but was replaced by silver and then by the ethyl group.

Ethyl 2 : 4-*Dinitrophenylethylcyanoacetate*.—From the preceding sodium derivative and silver nitrate in aqueous solution, the corresponding *silver* derivative was obtained as a red powder. This was dried, and treated with an excess of ethyl iodide; after some time, ether was added and the solution was filtered and evaporated. The residual red oil, which solidified, crystallised from alcohol in colourless plates, m. p. 98° (Found: C, 50·6; H, 4·7. $C_{13}H_{13}O_6N_3$ requires C, 50·8; H, 4·2%).

2 : 4-*Dinitrophenylacetonitrile* was obtained when ethyl 2 : 4-dinitrophenylcyanoacetate was boiled with dilute hydrochloric acid during 2—3 hours. It was isolated as an oil by means of ether and crystallised from carbon tetrachloride in yellow needles, m. p. 89° (Found: C, 46·1; H, 2·6; N, 20·2. $C_8H_5O_4N_3$ requires C, 46·4; H, 2·4; N, 20·3%). Its solution in hot water was colourless but became green on the addition of alkali.

Ethyl p-*nitrophenylcyanoacetate* was prepared in the same way as the dinitro-compound, a solution of 8 g. of *p*-nitrochlorobenzene in 20 c.c. of alcohol being used and what was unchanged being filtered off before the addition of nitric acid. The product, a brown oil which could not be solidified, was converted into its *sodium* derivative in the way described above (Found: Na, 9·0. $C_{11}H_9O_4N_2Na$ requires Na, 9·0%).

The crude ester was hydrolysed with dilute and with concentrated hydrochloric acid, which produced, respectively, *p*-nitrophenylacetonitrile, m. p. 114° (compare Radziszewski, *Ber.*, 1870, 3, 198), and *p*-nitrophenylacetic acid, m. p. 152° (Radziszewski, *Ber.*, 1869, 2, 209). The latter was further identified by a mixed melting-point determination with an authentic specimen.

Ethyl 2 : 4 : 6-*trinitrophenylcyanoacetate* also was prepared by the same method, a solution of 12·4 g. of picryl chloride in 60 c.c. of alcohol being used. The colourless product (8·7 g.) crystallised from alcohol–ligroin in faintly pink needles, m. p. 95°, which formed red and purple solutions in water and concentrated sulphuric acid, respectively (Found: C, 40·9; H, 3·2; N, 17·5. $C_{11}H_8O_8N_4$ requires C, 40·7; H, 2·5; N, 17·3%).

Ethyl αβ-*Di*-p-*nitrophenyl*-αβ-*dicyanosuccinate* (I; R = $C_6H_4\cdot NO_2$).—Ethyl *p*-nitrophenylcyanoacetate (1·5 g.) or its sodium derivative was refluxed with a solution of 2·5 g. of chromic anhydride in 20 c.c. of glacial acetic acid for ¾ hour. The white solid obtained by pouring the product into cold water crystallised from glacial acetic acid in colourless needles, m. p. 209° (Found: C, 57·2; H, 3·5; N, 12·1; *M*, cryoscopic in benzene, 451. $C_{22}H_{18}O_8N_4$ requires C, 56·7; H, 3·9; N, 12·1; *M*, 466), which gave a series of colour changes when warmed with alcoholic potash.

The ester was unattacked by hot concentrated hydrochloric or nitric acid, and was easily precipitated from the latter in a very pure state. Its structure was proved as follows: 4·5 g. of the silver derivative of ethyl *p*-nitrophenylcyanoacetate, prepared from the sodium derivative by the action of silver nitrate, were heated under reflux for ½ hour with a solution of 1·7 g. of iodine in ether. The silver iodide produced and the ether were removed and the residue, after being washed with alcohol to remove the excess of iodine, was crystallised twice from alcohol and once from glacial acetic acid; the needles thus obtained melted at 209°, alone or mixed with the specimen described above.

Ethyl 2 : 4-*dinitrobenzoylformate*, $C_6H_3(NO_2)_2\cdot CO\cdot CO_2Et$, was obtained by boiling a solution of 1·5 g. of ethyl 2 : 4-dinitrophenylcyanoacetate and 2·3 g. of chromic anhydride in glacial acetic acid for 1 hour. The colourless solid obtained by pouring the product into water was crystallised from alcohol; m. p. 89° (Found: C, 44·7; H, 3·35; N, 10·85; *M*, cryoscopic in benzene, 245. $C_{10}H_8O_7N_2$ requires C, 44·8; H, 3·0; N, 10·45%; *M*, 268). The *phenylhydrazone* separated from the mixture when 1 g. of the ester was heated on a water-bath for ¼ hour together with 10 drops of phenylhydrazine dissolved in dilute acetic acid; it crystallised from alcohol in golden needles, m. p. 170° (Found: N, 15·1. $C_{16}H_{14}O_6N_4$ requires N, 15·6%). A small amount of red substance, obtained on diluting the filtrate, melted, after recrystallisation from alcohol, at 139°. By fusing it with the product of m. p. 170° it was converted into the latter, indicating that it was probably another form of the phenylhydrazone.

Ethyl 2 : 4-*dinitrobromophenylcyanoacetate* was prepared by boiling the sodium derivative of ethyl 2 : 4-dinitrophenylcyanoacetate with excess of bromine dissolved in moist ether. It crystallised from alcohol in needles, m. p. 98° (Found: C, 36·9; H, 2·7; N, 12·3; Br, 21·9. $C_{11}H_8O_6N_3Br$ requires C, 36·9; H, 2·2; N, 11·7; Br, 22·3%). This compound was originally prepared by accident in an attempt to oxidise ethyl 2 : 4-dinitrophenylcyanoacetate by bromine instead of by chromic anhydride. That the bromine atom is in the ring was established by the preparation of the following oxidation product.

Ethyl 2 : 4-*dinitrobromophenylhydroxycyanoacetate*,

$C_6H_2Br(NO_2)_2\cdot C(OH)(CN)\cdot CO_2Et$,

was produced when ethyl 2 : 4-dinitrobromophenylcyanoacetate was treated with chromic anhydride under the conditions described for the previous oxidations. It crystallised from alcohol in colourless needles, m. p. 157° (Found: C, 35·3; H, 2·9; N, 12·6; Br, 21·4. $C_{11}H_8O_7N_3Br$ requires C, 35·3; H, 2·1; N, 11·2; Br, 21·4%).

Ethyl 2 : 4-*dinitrochlorophenylcyanoacetate* was prepared by passing chlorine into an aqueous solution of the sodium derivative of ethyl 2 : 4-dinitrophenylcyanoacetate until the red colour had been destroyed. It crystallised from alcohol in needles, m. p. 101° (Found: Cl, 11·3. $C_{11}H_8O_6N_3Cl$ requires Cl, 11·3%). The structure of this compound would appear to be sufficiently established by analogy with the corresponding bromo-derivative mentioned above. Its action with chromic anhydride is under investigation.

The authors wish to express their indebtedness to the Chemical Society for a grant to one of them (A. F.) which partly defrayed the expenses incurred in this work.

KING'S COLLEGE, LONDON, W.C. 2. [*Received, October* 16*th*, 1926.]

VIII.—*Studies in Optical Superposition. Part VIII. The* l-*Menthylamine, Brucine, and Strychnine Salts of Mucic and* allo*Mucic Acid.*

By THOMAS STEWART PATTERSON and JAMES DAVIDSON FULTON.

IN Part VII (J., 1926, 3224) and previous papers attempts were made to attack the problem of optical superposition by what seemed the simplest method capable of yielding positive results, namely, the preparation of esters formed from the *d*-, the *l*-, and the *i*-modifications of tartaric acid or some of its derivatives, with an active alcohol such as *l*-menthol or one of the methyl-*n*-hexylcarbinols. If the principle of optical superposition really holds, the mean of the rotations of such *d*- and *l*-compounds should be identical with that of the *i*-compound. This method sometimes presents considerable practical difficulties, and of course involves in the end result a possible summation of the experimental errors for the three different esters.

A method of obtaining further data on this problem would be the comparison of the rotations of esters of mucic and *allo*mucic acid, respectively, with active alcohols. These two acids are both optically inactive, their inactivity being due to compensation, in two different ways, of the activities due to the asymmetric carbon atoms. If the rotation of, say, *l*-menthyl mucate is different from that of *l*-menthyl *allo*mucate, this difference can hardly be ascribed to anything else than the different arrangement of the groups attached to the asymmetric carbon atoms in the mucic and *allo*mucic acids; and such a difference, we consider, would be a sound disproof of van 't Hoff's conception. Unfortunately, our attempts to prepare menthyl mucate and menthyl *allo*mucate by heating together the respective acids and the alcohol, under the influence of dry hydrogen chloride, have failed, but we have prepared some salts of these acids with active bases as described below. The salts of active acids are not so suitable for our purpose as the esters would have been; the results arrived at from rotation values obtained in aqueous solution, on the one hand, might easily be complicated by the influence of electrolytic dissociation, whilst, on the other, the solubility of such salts as we have been able to prepare is usually only slight in non-dissociating solvents. Nevertheless, we have determined the rotations of the brucine, the strychnine, and the *l*-menthylamine salts of mucic acid and of *allo*mucic acid, either in methyl alcohol or in benzyl alcohol. We prepared also the corresponding salts of nicotine, codeine, and morphine, but these were difficult to purify in a satisfactory manner and were not further examined. As a check on our results, the preparation of each salt and its optical examination were carried out twice; these preparations are indicated below as *A* and *B*.

allo*Mucic acid* was prepared according to Emil Fischer (*Ber.*, 1891, **24**, 2136) by heating mucic acid in aqueous pyridine solution in a copper autoclave. M. p. 172—173°.

Menthylamine Mucate.—To the acid (1 mol.) in hot water was added menthylamine (2 mols.), $\alpha_{5461}^{19°}$ (homogeneous: $l = 100$ mm.) $-35{\cdot}31°$, d 0·8574, $[\alpha]_{5461}^{19°}$ $-41{\cdot}2°$. This furnished a salt which, after two crystallisations from water, formed plates, m. p. 198° (decomp.) [Found: N, (*A*) 5·4, 5·4, (*B*) 5·4. $C_6H_{10}O_8,2C_{10}H_{21}N$ requires N, 5·4%]. $\alpha_{5461}^{19{\cdot}5°}$ (methyl alcohol: $c = 1$; $l = 400$ mm.) $= -1{\cdot}29°$ for *A* and $-1{\cdot}27°$ for *B*.

Menthylamine allo*mucate* was prepared in the same way as the mucate. Fine needles, m. p. 173° (decomp.) [Found: N, (*A*) 5·5, 5·4, (*B*) 5·4%]. $\alpha_{5461}^{19{\cdot}5°}$ (methyl alcohol: $c = 1$; $l = 400$ mm.) $=$ $-1{\cdot}26°$ for *A* and $-1{\cdot}24°$ for *B*.

The brucine salts were prepared similarly from purified brucine of m. p. 177—178° and $\alpha_{5461}^{17{\cdot}3}$ (ethyl alcohol: $c = 3{\cdot}008$; $l = 100$ mm).

= −2·97°, whence $[\alpha]^{17\cdot3^\circ}_{5461}$ = −98·74°; after recovery from the salts, its m. p. was 176° and $\alpha^{18^\circ}_{5461}$ (ethyl alcohol: $c = 3\cdot008$; $l = 100$ mm. = −2·94°, whence $[\alpha]^{18^\circ}_{5461}$ = −97·75°.

Brucine mucate, crystallised twice from water, formed needles which commenced to froth about 150° [Found in specimens dried for a long time in a vacuum over sulphuric acid: N, (*A*) 5·6, 5·8, (*B*) 5·7. $2C_{23}H_{26}O_4,C_6H_{10}O_8$ requires N, 5·6%]. In benzyl alcohol ($c = 5$; $l = 400$ mm.), $\alpha^{17^\circ}_{5461}$ for *A* = +0·27° and $\alpha^{20^\circ}_{5461}$ for *B* = +0·23°, whence $[\alpha]^{17^\circ}_{5461}$ and $[\alpha]^{20^\circ}_{5461}$ = + 1·35° and +1·15°, respectively. After some time, a fine precipitate settled on the walls of the tube and the rotation altered.

Brucine allo*mucate* formed needles which, after two crystallisations from water, decomposed at 170°, softening at a lower temperature [Found: N, (*A*) 5·7, 5·8, (*B*) 5·7%]. In benzyl alcohol ($c = 5$; $l = 400$ mm.), $\alpha^{17^\circ}_{5461}$ for *A* = −0·22° and $\alpha^{20^\circ}_{5461}$ for *B* = −0·19°, whence $[\alpha]^{17^\circ}_{5461}$ and $[\alpha]^{20^\circ}_{5461}$ = −1·10° and −0·95°, respectively.

The *strychnine* salts were prepared from purified strychnine of m. p. 284° and $\alpha^{20^\circ}_{5461}$ (chloroform: $l = 100$ mm.; $c = 5\cdot02$) = −8·61°, whence $[\alpha]^{20^\circ}_{5461}$ = −171·5°; after recovery from the salts, its m. p. was unchanged and $[\alpha]^{19\cdot5^\circ}_{5461}$ = −169·7°.

Strychnine mucate, twice recrystallised from water, formed fine needles which became brown at 200° and decomposed at 273°. The compound had previously been prepared by Ruhemann and Dufton (J., 1891, **59**, 750) [Found: N, (*A*) 6·35, 6·4, (*B*) 6·4. Calc. for $2C_{21}H_{22}O_2N_2,C_6H_{10}O_8$: N, 6·4%]. $\alpha^{17\cdot5^\circ}_{5461}$ (benzyl alcohol: $l = 400$ mm.; $c = 3\cdot5$) for *A* = +1·11°, whence $[\alpha]^{17\cdot5^\circ}_{5461}$ = +7·93°, and $\alpha^{21\cdot5^\circ}_{5461}$ (benzyl alcohol: $l = 400$ mm.; $c = 5$) for *B* = +1·06°, whence $[\alpha]^{21\cdot5^\circ}_{5461}$ = + 7·57°.

Strychnine allo*mucate*, twice crystallised from water, formed needles turning brown at 189°, and decomposing at 269° [Found: N, (*A*) 6·4, 6·45, (*B*) 6·4%]. In benzyl alcohol ($c = 3\cdot5$; $l = 400$ mm.), $\alpha^{17\cdot5^\circ}_{5461}$ for *A* = + 0·99° and $\alpha^{21\cdot5^\circ}_{5461}$ for *B* = + 0·96°, whence $[\alpha]^{17\cdot5^\circ}_{5461}$ and $[\alpha]^{21\cdot5^\circ}_{5461}$ = +7·07° and +6·86°, respectively.

The results of these experiments are tabulated:

Specific Rotation for Mercury Green Light. Temperature about 20°.

	Menthylamine.	Δ.	Brucine.	Δ.	Strychnine.	Δ.
First series.						
Mucic acid	−32·25°	0·75°	+1·35°	2·45°	+7·93°	0·86°
*allo*Mucic acid	−31·50		−1·10		+7·07	
Second series.						
Mucic acid	−31·75	0·75	+1·15	2·11	+7·57	0·71
*allo*Mucic acid	−31·00		−0·96		+6·86	

Regarding these results, it may be noted particularly that the rotations of the brucine and strychnine salts of mucic and *allo*mucic acid are remarkably low in view of the highly active character of the bases and the inactivity of the acids. This might well suggest the idea that in combination with certain active bases the asymmetric carbon atoms of the acid molecule no longer neutralise each other in pairs, but that the acid part of the molecule has become active and is contributing to the rotation. This, if it be the case, is, of course, in strong opposition to the principle of optical superposition. A similar observation was made in Part V of this series (J., 1924, **125**, 578), where the specific rotation, $[\alpha]_{5461}^{17^\circ}$, of *d*-*sec*.-octyl *i*-tartrate was found to be only 0·18°. The menthylamine salts show a similar tendency, but not so markedly.

It will be seen from the third column of the table that the difference found between the specific rotations of the menthylamine salts of mucic and *allo*mucic acid is only small, 0·75°, but it is the same in both series, and greater, although not much, than the difference which was found between the rotations for like salts of one of the acids in the two series of experiments. It is, therefore, presumably greater than the experimental error.

The difference for the brucine salts is also nearly the same in the two series of experiments, but it is specially remarkable that the two salts are active in opposite senses. This seems to be a really strong argument against the principle of optical superposition. With reference to the strychnine salts, it may be noted, firstly, that the rotations are both positive, and secondly, that although the absolute difference is not very great, it is at least twice the probable experimental error and fairly large in proportion to the actual rotations of the individual compounds.

Thus, although the results for the menthylamine and strychnine salts are hardly as definite as might be desired, they certainly do not seem to support the idea that the configuration of mucic acid has exactly the same effect as that of *allo*mucic acid in determining the rotation of compounds formed from these acids and one and the same active base, whilst the results with the brucine salts are definitely in conflict with van 't Hoff's supposition.

UNIVERSITY OF GLASGOW. [*Received, November 30th*, 1926.]

IX.—*Optical Activity and the Polarity of Substituent Groups. Part VI. Optically Active Acids and Bases.*

By HAROLD GORDON RULE.

IN the first paper of this series (J., 1924, **125**, 1121), it was shown, from a consideration of the relative directive effects of a number of substituents on benzene substitution, that the substituents could be arranged in a *polar series* representing a gradual transition from those of high positive polarity through the comparatively non-polar groups to those of high negative polarity. This series was also found to correspond with the influence of the same substituents on the rotatory powers of certain aliphatic and aromatic compounds, special reference being made to the menthyl esters of ortho-substituted benzoic acids. A theoretical justification for this series was based on the views of Sir J. J. Thomson on the nature of substitution in organic compounds (*Phil. Mag.*, 1923, **46**, 497).

In the main, these conclusions have been supported by further experiments with the menthyl and *sec.*-β-octyl esters of *o*-substituted benzoic acids (Rule and Smith, J., 1926, 553; Rule and Numbers, *ibid.*, 2116), although where the substituents are separated from the asymmetric atom by a longer non-conjugated chain their influence on the rotatory power is more closely related to their *general effect* as deduced from data referring to the dissociation constants of acids. Under the latter heading may be mentioned the derivatives of active bases investigated by Betti (*Gazzetta*, 1923, **53**, 417) and the menthyl and *sec.*-β-octyl esters of monosubstituted acetic acids (Rule and Smith, J., 1925, **127**, 2188; Rule and Mitchell, J., 1926, 3202). The deductions previously drawn from Thomson's views on *m*- and *p*-disubstituted benzenes have not been confirmed, however, and from an investigation on the inductive capacities of *o*-, *m*-, and *p*-disubstituted benzenes recently carried out in these laboratories, Kerr (*Phil. Mag.*, in the press) concludes that Thomson's suggestions only hold in their original simplicity for compounds of this type in which the two substituents are identical.

Now if the properties of compounds are affected in the manner indicated above by the polarity of substituent groups, it would be anticipated that changes of an even more pronounced character would follow the introduction into the molecule of ionisable complexes which are capable of assuming an actual electrical charge. It is an accepted fact that an ionised complex exerts a powerful influence on substitution in the benzene nucleus, and that the course of this reaction varies with the sign of the charge. For example, although aniline under ordinary conditions substitutes in the *o*-, *p*-positions, it may be nitrated in the *m*-position by using it in the form of aniline sulphate dissolved in a large excess of sulphuric acid. The positively charged ionic complex $\cdot NH_3^+$ thus behaves as a positive or *m*-directive substituent. On the other hand, benzoic acid, which brominates slowly in the *m*-position, may be rapidly converted into the *o*- and *p*-derivatives by chlorinating the sodium salt in aqueous solution (Lossen, D.R.-P. 146174). Here the negatively charged complex $\cdot CO\cdot O^-$ ranges itself with the negative or *o*-, *p*-directive substituents. The parallel between the influence of substituents on the nitration of a mono-substituted benzene and on the optical activity of esters of *o*-substituted benzoic acids is illustrated in the following table, where (*a*) represents the percentage of *m*-compound formed, (*b*) percentage of *p*-compound, (*c*) molecular rotations of the menthyl esters, and (*d*) molecular rotations of the *sec.*-β-octyl esters, in so far as these values have been determined.

Table of Substituent Influence.

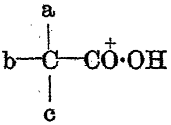
	NH_3^+.	NO_2.	CO_2H.	COMe.	H.	Me.	I.
a	Chiefly meta	93	76	55	—	3·1	—
b		0·4	1·2	—	—	41	66
c	—	381°	332°	261°	239°	231°	237°
d	—	122°	(90—117°*)	—	78°	—	—

	Br.	Cl.	F.	$CO\cdot O^-$.	OMe.	NMe_2.
a	0·3	—	0·2			
b	62	70	87	(Chiefly para and ortho.)		
c	205°	195°	194°	180°	148°	101°
d	—	47°*	—	—	33°	—

* Rule, Numbers, and Paterson, unpublished results.

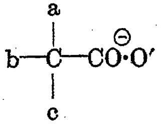
The parallel is a very complete one, and particular attention may be directed to the difference in the behaviour of the positive carboxyl group and the negatively charged $\cdot CO\cdot O^-$ complex. The value of 180° is quoted for the rotation of the sodium salt of menthyl hydrogen phthalate in 5% aqueous solution (Kenyon and Pickard, J., 1915, **107**, 58), but it is probable that this falls to a still lower limiting value at greater dilutions. No figures are yet available for the rotation of menthyl *o*-dimethylaminobenzoate in acid solution. It may, however, be predicted that this will be higher than that for the free basic ester, and probably higher than the value for the unsubstituted menthyl benzoate, if the hydrochloride is sufficiently ionised under the conditions of experiment.

The influence of an ionisable group should also be recognisable in a simple type of compound in which the remaining three groups attached to the asymmetric atom are of a comparatively non-polar character. In this connexion, it is common knowledge among workers with optically active substances that the rotations of simple active acids and bases often diminish in magnitude and frequently undergo a reversal of sign when the compounds are converted into the ionised state. This is precisely what might be expected, particularly if the acidic or basic group is the only group of high polar character in the molecule.

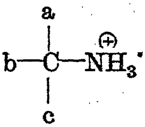


$$\mathrm{b{-}\overset{a}{\underset{c}{C}}{-}C\overset{+}{O}{\cdot}OH}$$

and

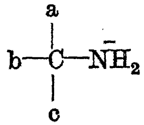


$$\mathrm{b{-}\overset{a}{\underset{c}{C}}{-}C\overset{\ominus}{O}{\cdot}O'}$$



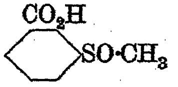
$$\mathrm{b{-}\overset{a}{\underset{c}{C}}{-}\overset{\oplus}{N}H_3{}^{\cdot}}$$

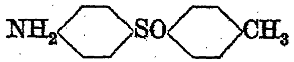
and



$$\mathrm{b{-}\overset{a}{\underset{c}{C}}{-}\overset{-}{N}H_2}$$

Among optically active acids undergoing a reversal of this kind may be mentioned the lactic, glyceric, and methoxysuccinic acids. Phenylpropylacetic acid (Pickard and Yates, J., 1909, 95, 1011), having a molecular rotation of $[M]_D = 140{\cdot}7°$ in benzene and 104·7° in chloroform, gives a sodium salt of $[M]_D = 5{\cdot}0°$ in water. Benzylmethylacetic acid increases somewhat in rotation on being converted into its sodium salt. Numerous salts of *d*-valeric acid are described in the literature, but no mention is made of their rotatory power. A specimen of commercial valeric acid in the author's possession, however, had a specific rotation almost exactly double that of the corresponding sodium salt, when both were examined in a 10% solution in aqueous alcohol. The tendency in this case is therefore towards a reversal of sign. The interesting optically active sulphoxides prepared by Harrison, Kenyon, and Phillips (J., 1926, 2079), in which the ionisable groups are separated from the asymmetric sulphur atom by a benzene nucleus, behave in the same manner. *d*-*m*-Carboxyphenyl methyl sulphoxide has a lower rotation in the form of its sodium salt, and *l*-4′-amino-4-methyldiphenyl sulphoxide suffers a reversal of the sign of rotation in hydrochloric acid solution.





Other typical optically active bases which show a reversal of sign on being converted into their hydrochlorides are lævorotatory amylamine and *l*-nicotine. On the other hand, *d*-butyl*iso*butylacetic acid is recorded as having a specific rotation of + 6·3° in xylene, + 6·0° in alcohol, and + 7·1° in an equivalent amount of aqueous sodium hydroxide (Fischer, Holzapfel, and Gwinner, *Ber.*, 1912, **45**, 250). No figures are available for the salt and the acid in the same solvent.

In the majority of cases, the ionisation of an active carboxylic acid appears to lead to a smaller change in rotatory power than the ionisation of an active base. Probably one factor contributing towards the weaker effect of the electrolytically dissociated carboxyl group is that the atom bearing the charge is one remove further away from the asymmetric centre than that in the corresponding base.

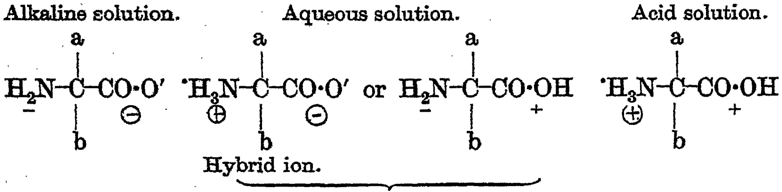
A more definite example of the change in the polar influence of the amino-group on ionisation is to be found in the rotatory powers of derivatives of active amyl alcohol, although it is doubtful if some of these have yet been obtained in a state of optical purity.

Molecular Rotations of Amyl Derivatives, $C_5H_{11}X$.

X.	$\cdot NH_3^+$.	CO_2H.	I.	Et.	Br.	Cl.	OMe.	OH.	NH_2.
[*M*]	+11·20°	+10·5°	+11·17°	+6·2°	+5·6°	+1·8°	+0·41°	−5·1°	−5·2°

An examination of the figures reveals a close analogy with those relating to the menthyl benzoates and to benzene substitution. Here again the substituents arrange themselves into the polar series, having at the one end the positively charged ionic complex $\cdot NH_3^+$ and the carboxyl group, and at the other end the negative amino- and hydroxyl groups. The value quoted for the carboxylic compound is certainly too low (compare J., 1924, **125**, 1121) and possibly the rotation of the amine hydrochloride would also be increased under conditions leading to more complete ionisation. These figures illustrating the reversal in the influence of the amino-group when ionised supplement those recorded above for the carboxyl group in the menthyl benzoates.

Additional support for this explanation of the behaviour of optically active acids and bases may be found in the variations undergone by the rotatory powers of active amino-acids in alkaline, neutral and acid solution. An amino-acid in aqueous solution is in only a very slightly ionised state. On making such a solution alkaline, the result, on the whole, is to convert the positive carboxyl group more or less completely into the negatively charged complex $\cdot CO\cdot O'$. On the other hand, the addition of hydrochloric acid to the aqueous solution results in the more complete ionisation of the amino-group, transforming it from a negative substituent into one of positive polarity. These changes go hand in hand with alterations in rotatory power, as may be seen from the following figures referring to the specific rotations of aspartic acid and asparagine. In the formulæ an encircled positive or negative sign represents an ionised complex.



$$\underset{-}{H_2N}-\overset{a}{\underset{b}{C}}-CO\cdot\underset{\ominus}{O'} \quad \underset{\oplus}{\cdot H_3N}-\overset{a}{\underset{b}{C}}-CO\cdot\underset{\ominus}{O'} \text{ or } \underset{-}{H_2N}-\overset{a}{\underset{b}{C}}-\underset{+}{CO\cdot OH} \quad \underset{\oplus}{\cdot H_3N}-\overset{a}{\underset{b}{C}}-\underset{+}{CO\cdot OH}$$

d-Aspartic acid.	$-9{\cdot}02°$ (1 mol. NH_3)	$+4{\cdot}36°$	$+30{\cdot}0°$ (1 mol. HCl)
l-Asparagine.	$-8{\cdot}64°$ (1 mol. NaOH)	$-5{\cdot}30°$	$+26{\cdot}4°$ (1 mol. HCl)

Exceptional behaviour is shown by *l*-leucine, which is recorded as being lævorotatory in aqueous solution and dextrorotatory in both acid and alkaline solutions. Taken in conjunction with the case of *d*-butyl*iso*butylacetic acid already mentioned, this suggests that there is a disturbing factor in the rotatory powers of these two acids, due to the critical length of the butyl chain.

It is evident that the presence or absence of groups of marked polarity is one of the main factors governing the rotatory power of an optically active compound, and already it seems possible to discern at least three ways in which their influence may be brought to bear on the asymmetric atom. The polar influence may be intramolecular and transmitted either through the chain of atoms or through space, as in the case of the menthyl benzoates and amyl derivatives quoted. A second effect, studied by Frankland, Pickard and Kenyon, Hilditch, and others, may lead to a sudden change in activity as the chain attached to the asymmetric centre attains a length of 5, 10, or 15 atoms. This effect is apparently due to the end of the chain coming into close proximity to the asymmetric atom and is therefore intramolecular and transmitted through space. In addition, it is probable that polar groups, whether present in the asymmetric compound or in the solvent, also exert an influence on neighbouring molecules, leading to corresponding changes in rotatory power. Some evidence on this point is provided by the fact that the substituents of the series $H < Me < OMe < Cl < Br < I$ exert a graded influence in the sense indicated on the molecular rotations of the *sec.*-β-octyl acetates, $CH_2X\cdot CO\cdot O\cdot C_8H_{17}$, and that the influence of the solvents C_6H_5X on each of these esters is given by practically the same sequence, *viz.*, $Me < H < OEt < Cl < Br < I$ (Rule and Mitchell, J., 1926, 3202).

Summary.

1. It has previously been shown that substituents may be arranged into a polar series representing a gradual transition from high positive, through neutral, to high negative polarity, and that this series corresponds to the relative influence of the substituents on

benzene substitution and the rotatory power of a number of optically active compounds.

2. It is now pointed out that the positively charged ionic complex $-NH_3^{\cdot}$ ranges itself with the positive substituents and the negatively charged complex $-CO{\cdot}O'$ with the negative substituents in their influence on rotatory power and benzene substitution.

3. This extension of the original theory is shown to explain the behaviour of a number of optically active bases, acids, and amino-acids on ionisation.

4. Three ways are suggested by which the polar effect may be transmitted to the asymmetric atom.

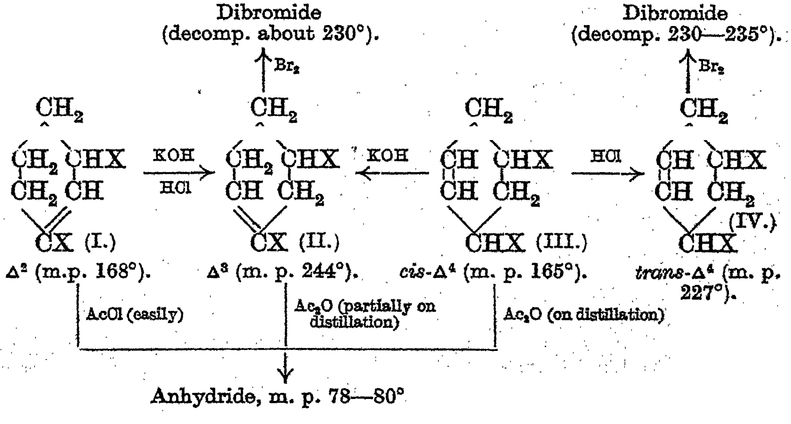
UNIVERSITY OF EDINBURGH.

[*Received, November 27th*, 1926.]

X.—*The Chemistry of the Glutaconic Acids. Part XXI. Non-formation of Δ²-Tetrahydro*iso*phthalic Acid by Reduction of* iso*Phthalic Acid.*

By ERNEST HAROLD FARMER and HENRY LORIMER RICHARDSON.

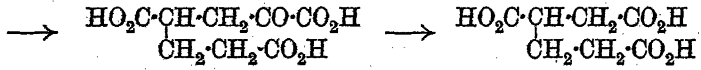
IT was shown recently (Farmer and Richardson, J., 1926, 2173) that the Δ²-tetrahydro*iso*phthalic acid of Perkin and Pickles (J., 1905, **87**, 293) does not possess glutaconic characteristics and should, on account of the ease with which it gives an anhydride and the nature of its oxidation products, be represented by the *cis*-Δ⁴-formula. This correction quite precludes the possibility of a normal chemical relationship existing between the four tetrahydro-isomerides described by Perkin and Pickles: each of the possible ways of redistributing the formulæ involves a departure from customary chemical behaviour more serious than that connected with anhydride formation in the original scheme (below).



The most direct way of obtaining the necessary evidence for a reallotment of formulæ would appear to be oxidation of the remaining three isomerides. There are, however, two points which stand out from the evidence already recorded, and these have considerable importance in view of the later experimental results. The first concerns the conversion of the *cis*- into the *trans*-Δ^4-acid shown above; since the alleged *cis*-Δ^4-acid must have a structure other than that assigned to it in the scheme, the probability that the acid derived therefrom (by treatment with hydrochloric acid) is the *trans*-Δ^4-isomeride is greatly diminished. Secondly, the close similarity between the alleged Δ^3- and *trans*-Δ^4-acids and their similar behaviour on bromination strongly suggest their identity—a contingency which would reduce the number of isomerides isolated to three.

The main product of reduction of *iso*phthalic acid under the conditions described by Perkin and Pickles is the substance now regarded as the *cis*-Δ^4-acid (formerly Δ^2). Along with it appears a small quantity of an isomeric acid, m. p. 244° (Perkin and Pickles's Δ^3-acid): this is obviously not a primary product of reduction, since it is produced in still smaller quantity when the temperature and alkalinity during reduction are diminished; also it is produced quite readily by boiling the pure *cis*-Δ^4-acid with alkali. The constitution of this substance follows from its oxidation by ozone to β-carboxyadipic acid, and therefore the Δ^3-formula assigned to it by Perkin and Pickles is correct.

(II.)



$$\longrightarrow\ \begin{array}{l}HO_2C{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot}CO{\cdot}CO_2H\\ \qquad\ CH_2{\cdot}CH_2{\cdot}CO_2H\end{array}\ \longrightarrow\ \begin{array}{l}HO_2C{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot}CO_2H\\ \qquad\ CH_2{\cdot}CH_2{\cdot}CO_2H\end{array}$$

The second primary product of the reduction—regarded by Perkin and Pickles as the *cis*-Δ^4-acid—must, therefore, if it is a tetrahydro*iso*phthalic acid, be either the true Δ^2- or the *trans*-Δ^4-form; both structures are difficult to reconcile with the recorded properties.

Considerable quantities of carefully purified *iso*phthalic acid have been reduced during these experiments, and the separation methods of Perkin and Pickles employed in isolating the products. We have been quite unable to satisfy ourselves that any portion of the reduction product contained a third isomeride. Not only has a third isomeride not been isolated, but oxidation of the entire residue after separation of the bulk of the pure Δ^3- and *cis*-Δ^4-acids has failed to yield any recognisable trace of adipic (or glutaric) acid.*

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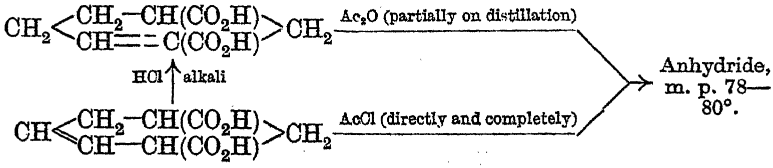
* Various portions approximating in melting point to that recorded for the "*cis*-Δ^4"-acid have been oxidised separately: one of these oxidations was referred to in a footnote of the previous memoir (p. 2173). Invariably the main product was tricarballylic acid.

The absence of the true Δ^2-acid from the reduction product therefore appears certain, and the remaining possibility, the occurrence of the *trans*-Δ^4-acid, is discounted on the following grounds: (1) non-isolability in the pure condition; (2) the inferior melting points of the residual portions of the reduction product; and (3) the strong indication afforded by the nature and analysis of the residues as to their consisting of mixtures of the Δ^3- and *cis*-Δ^4-acids with small quantities of non-isomeric impurities.* These results render the identity of Perkin and Pickles's Δ^3- and *trans*-Δ^4-forms all the more probable, and the relationship of the two veritable tetrahydro-acids, as represented below, is one which renders the direct conversion of the *cis*- into the *trans*-Δ^4-acid improbable of attainment.



$$CH_2{<}\begin{matrix}CH_2{-}CH(CO_2H)\\CH{=\!=}C(CO_2H)\end{matrix}{>}CH_2 \qquad CH{<}\begin{matrix}CH_2{-}CH(CO_2H)\\CH{-}CH(CO_2H)\end{matrix}{>}CH_2$$

Ac₂O (partially on distillation)
HCl
alkali
AcCl (directly and completely)
Anhydride, m. p. 78—80°.

It was noted by Perkin and Pickles that the dihydro*iso*phthalic acids appeared to be absent from their reduction products: this was the case also in our experiments. Yet the reduction may be regarded as normal in that it effects the hydrogenation of two CH:CH·CO groups. Further reduction experiments are being carried out and at the suggestion of Professor W. H. Perkin the synthesis of the Δ^2-tetrahydro-acid is being attempted.

EXPERIMENTAL.

Oxidation of Δ^3-*Tetrahydro*iso*phthalic Acid.*—The acid, m. p. 243—244°, was prepared by boiling the *cis*-Δ^4-acid (Perkin and Pickles's Δ^2-acid) with 30% aqueous potash and recrystallising the product from water (with the aid of charcoal) and from formic acid. A solution of 5 g. of it in a slight deficit of aqueous sodium carbonate was treated with ozonised oxygen for 20 hours; the product, after being freed from ozone by a rapid stream of air, gave a strong, aldehydic reaction with Schiff's reagent and with ammoniacal silver nitrate, but yielded no semicarbazone. The precipitate of *iso*phthalic acid (0·25 g., identified as methyl ester) obtained on acidification was removed and the filtrate was neutralised with alkali and carefully treated with dilute permanganate solution at 0° until the latter was no longer reduced. From the mixture, worked up in the usual way, ether extracted about 4 g. of a crystalline acid,

---

* Nevertheless it has not been possible to demonstrate conclusively that the *trans*-Δ^4-acid is absent. It might quite well be produced in the reduction process and would yield tricarballylic acid on oxidation.

m. p. 110—115°; this, after recrystallisation from acetone–benzene and ethyl acetate, melted at 121° [Found: C, 44·3; H, 5·3; *M*(tribasic), 192. Calc. for $C_7H_{10}O_6$: C, 44·2; H, 5·3%; *M*, 190], alone or mixed with β-carboxyadipic acid prepared by Haworth and King's method (J., 1914, **105**, 1350).

Attempted Isolation of Perkin and Pickles's cis-Δ^4-*Acid.*—Since the Δ^2-acid of Perkin and Pickles is the true Δ^4-acid (almost certainly *cis*), the *cis*-Δ^4-acid of these authors must, if it represent a single isomeride of this series, be either the *trans*-Δ^4- or the Δ^2-form. On oxidation, the former of these should pass into tricarballylic acid, and the latter into adipic acid.

The earlier stages of Perkin and Pickles's calcium-salt method (*loc. cit.*, p. 302) for separating the reduction products of *iso*phthalic acid were followed. The calcium salt mother-liquors (the source of the "*cis*-Δ^4"-acid) yielded a glassy mass on evaporation. Fractional crystallisation of the acid regenerated from this (as described, *loc. cit.*, p. 311) yielded acid fractions of various melting points. Since samples approximating in m.p. to the recorded melting point "about 165°" * yielded considerable quantities of tricarballylic acid on oxidation with ozone, it was obvious that they did not consist of pure or nearly pure Δ^2-acid; the result, however, does not conflict with the Δ^4-structure for at least a portion of the material.

The acids obtained from a large quantity of the glassy calcium salts were regenerated and when solid were dissolved in hot water; almost pure Δ^3-acid separated on standing. The acids in the mother-liquor were reconverted into the calcium salts; a quantity of the less soluble calcium salt of the "Δ^2"-(true *cis*-Δ^4-)acid could then be removed. Again the mother-liquor yielded a glassy mass on evaporation. The alternate removal of Δ^3-acid and true *cis*-Δ^4-acid (as acid and calcium salt, respectively) was continued until less than 1 g. of acid (m. p. 165—200° after recrystallisation from formic acid) remained. This substance depressed the melting point of the pure *cis*-Δ^4-acid and gave very inferior analytical figures; it could not be regarded as a pure substance.

The acid material from the calcium salt mother-liquor appeared, therefore, to consist very largely of the Δ^3- and *cis*-Δ^4-acids. Of these, the former could readily be purified and identified beyond doubt; the purity of the latter, now free from all but the merest trace of the former, was not equally certain. Consequently, in demonstrating the absence of the Δ^2-acid (below) this portion of the reduction product was included.

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* The above authors state that the melting point must be regarded as approximate only, as the acid obviously may have contained traces of "Δ^2"-tetrahydro*iso*phthalic acid.

Absence of the Δ^2-Acid from the Reduction Products.—The whole of the acid products derived from the calcium salt mother-liquors, except that portion removed as pure Δ^3-acid (above), was dissolved in aqueous sodium carbonate and treated with ozone as described above. Ether extracted from the acidified solution a sticky solid, m. p. 163—169° after recrystallisation from formic acid. This substance (amounting to about one-third of the material taken), which appeared to be slightly impure *cis*-Δ^4-acid (m. p. 172°) that had escaped oxidation, was re-submitted to oxidation (below). The aqueous mother-liquor, which gave a strong aldehyde reaction, was carefully reoxidised with dilute permanganate solution at 0°. The manganese-free liquor therefrom was acidified and evaporated to dryness in a vacuum. Extraction of the residue with acetone yielded a gummy mass, an aqueous solution of which, on concentration, deposited crystals of tricarballylic acid, representing nearly one-half of the material taken. No trace of adipic or glutaric acid could be isolated from the small residue.

The unoxidised portion (above) was combined with the ethereal extract of all the mother-liquors and porous tiles likely to contain acid derived from the more soluble calcium salt, and the whole was oxidised as before. The ethereal extract of the acidified product was a gummy mass (representing about 45% of the material taken). This and the aqueous mother-liquor were separately oxidised with permanganate. The former yielded a very small quantity of *iso*phthalic acid and some acid material readily soluble in water; the latter also yielded readily soluble, acid material. From the combined water-soluble portions, on concentration, tricarballylic acid separated in considerable quantity. No trace of adipic or glutaric acid could be isolated from the residue. Thus, whilst there is no evidence of the presence of the true Δ^2-acid in these portions of the *iso*phthalic acid reduction product, it is possible, although improbable, that a portion of the tricarballylic acid was derived from the *trans*-Δ^4-acid.

The authors desire to express their thanks to the Chemical Society for a grant to one of them (H. L. R.) which has partly defrayed the cost of this research.

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[*Received, December 2nd,* 1926.]

XI.—*The Rearrangement of the Alkylanilines.*

By Wilfred John Hickinbottom.

When an alkylaniline is heated in a sealed tube with hydrogen chloride (Hofmann and Martius, *Ber.*, 1871, 4, 742) or certain metal chlorides (Reilly and Hickinbottom, J., 1920, **117**, 103) migration of the alkyl group from nitrogen to the nucleus occurs. This change has been regarded by Reilly and Hickinbottom as a true isomerisation and by Beckmann and Correns (*Ber.*, 1922, 55, 852; compare also Howard and Derrick, *J. Amer. Chem. Soc.*, 1924, 46, 166) as consequent to dissociation of alkyl halide from the alkylaniline hydrochloride.

If the latter assumption is correct, the formation of *p*-aminoalkylbenzene should be diminished or prevented under conditions which favour the removal of alkyl halide. It is necessary to select the conditions so that side reactions may be either detected or eliminated.

The behaviour of ethylaniline and butylaniline on heating in presence of metal chlorides in open tubes has been examined. If the rearrangement is due to the intermediate formation of alkyl chloride, either through the presence of traces of water (compare Chapman, J., 1925, **127**, 2818),

$$2NHR{\cdot}C_6H_5 + CdCl_2 + H_2O \longrightarrow 2RCl + 2C_6H_5{\cdot}NH_2 + CdO$$
$$\longrightarrow 2R{\cdot}C_6H_4{\cdot}NH_2 + CdCl_2 + H_2O,$$

or by exchange of halogen from metal to alkyl group, the product should contain a high proportion of aniline and a considerable quantity of metal or metal oxide. It is assumed that the reaction between the benzene nucleus and alkyl halide is not accelerated by metal chlorides. This assumption is supported by the observation that aluminium chloride or zinc chloride has no appreciable effect on the rearrangement of methylaniline hydrochloride (Beckmann and Correns, *loc. cit.*).

Butylaniline and ethylaniline, when heated in open tubes with the chloride of cobalt, cadmium, or manganese at 220—290°, gave *p*-aminobutyl- and *p*-aminoethyl-benzene, respectively. No alkyl chloride was detected during the reaction, and the yield of aniline was negligible. The rearrangement proceeded readily even when precautions were taken to exclude traces of moisture. When zinc chloride was used as a promoter, the principal product was *p*-aminoalkylbenzene; small quantities of aniline and more complex primary amines were also present.

To refute still further the view that the reaction may proceed according to the scheme given above, the behaviour of the alkylaniline hydrochlorides on being heated in open tubes was compared with that of the free secondary amines in presence of metal chlorides under similar conditions. Ethylaniline hydrochloride, heated at 220—290° in open tubes, gave chiefly aniline, but also a small quantity of another primary amine. Dry butylaniline hydrochloride under similar conditions yielded *p*-amino-*n*-butylbenzene. The presence of small quantities of volatile impurities in the hydrochloride resulted in the production of aniline and *n*-butyl chloride.

The isomerisation of alkylanilines may be effected also by heating them in open tubes with metal salts other than chlorides.

EXPERIMENTAL.

In most of the experiments the amine hydrochloride or the mixture of amine and metallic salt was heated to the required temperature in a long, vertical test-tube. The volatile products could be collected when desired.

The secondary amines were carefully freed from traces of primary and tertiary amines.

Rearrangement of Alkylanilines in Presence of Metal Chlorides.

(a) *Formation of* p-*Aminoethylbenzene from Ethylaniline.*—(1) *In presence of cobalt chloride.* Dry ethylaniline (15 g.) and anhydrous cobalt chloride (7 g.), heated at 240—270° for 12 hours in a tube fitted with phosphoric oxide guard-tubes, yielded a solid, bluish-green mass of *p*-aminoethylbenzene cobaltochloride mixed with a small quantity of unchanged secondary amine. The pure cobaltochloride separated from methyl alcohol as a bright blue, crystalline mass.

In other experiments the ethylaniline was dried over fused potassium hydroxide or phosphoric oxide and distilled on to anhydrous cobalt chloride in an apparatus open to the air only through a train of phosphoric oxide tubes. The rearrangement under these conditions proceeded readily.

When cobalt chloride was used as a promoter a varying quantity of a grey, magnetic powder remained when the reaction product was dissolved in methyl alcohol (Found: Co, 96·8%. Found in the powder from another experiment in which the materials had not been dried: Co, 93·0%).

(2) *In presence of zinc chloride.* Ethylaniline (40 g.) was heated with half its weight of fused zinc chloride in a long-necked flask at 210° for 8 hours and finally for 2 hours at 260°. The product, triturated with an aqueous solution of zinc chloride and freed from the uncombined amine by washing with ether, yielded the primary amines as zincichlorides. Distillation of the free primary amines, followed by fractional crystallisation of the sulphates, furnished

pure *p*-aminoethylbenzene sulphate (14 g.) and a further quantity contaminated with aniline sulphate. There was a residue of amines of higher molecular weight.

p-Aminoethylbenzene was identified in the form of its acetyl derivative—slender needles from water, m. p. 95° (Beilstein and Kuhlberg, *Annalen*, 1870, **156**, 208)—and its sulphate (Found: H_2SO_4, 28·4. Calc.: H_2SO_4, 28·8%). Replacement of the amino-group by chlorine and oxidation of the chlorohydrocarbon by alkaline permanganate yielded *p*-chlorobenzoic acid.

(b) *Formation of* p-*Amino*-n-*butylbenzene from* n-*Butylaniline*.—(1) *In presence of cobalt chloride.* A mixture of *n*-butylaniline and cobalt chloride, maintained at 230—240° for 15 hours, gave a product consisting of *p*-amino-*n*-butylbenzene and some unchanged secondary amine. No butyl chloride was detected.

(2) *In presence of zinc chloride.* Butylaniline (35 g.) and zinc chloride (19 g.), heated at 220—230° for 11 hours, yielded *p*-amino-*n*-butylbenzene (18 g.), impure aniline (1·8 g.), primary amines of higher molecular weight (4·5 g.), and secondary amines (8 g.).

(3) *In presence of manganese chloride.* The product after 15 hours' heating at 240—250° contained approximately 30% of *p*-amino-*n*-butylbenzene. No appreciable quantity of other primary amines was present.

(4) *In presence of cadmium chloride.* Dry butylaniline and anhydrous cadmium chloride, heated at 190° for 4 hours and then at 250—290° for 14 hours, gave *p*-amino-*n*-butylbenzene cadmichloride, some secondary amine, and a trace of a tertiary amine.

p-Amino-*n*-butylbenzene was isolated from the reaction mixture usually through its insoluble zincichloride, and was freed from other primary amines by fractional crystallisation of its sulphate. It was identified by comparison of its benzenesulphonyl derivative, m. p. 78°, and acetyl derivative with authentic specimens.

Behaviour of Alkylaniline Hydrochlorides on Heating.

Ethylaniline Hydrochloride.—The dry hydrochloride, heated in an open tube at 200—220° for 15 hours, gave a pale yellow, soft, crystalline mass (Found: Cl, 15·7%) consisting of a mixture of primary and secondary amines with a small quantity of diethylaniline. The primary amines comprised aniline (80% was isolated in a pure state), and another amine not definitely identified. In many other experiments, the principal product was aniline, although the temperature and duration of heating were varied considerably.

Butylaniline Hydrochloride.—No butyl chloride was obtained when the dry hydrochloride was heated at 230—235° for 18 hours. The product was *p*-amino-*n*-butylbenzene and a small quantity of aniline.

The presence of free hydrogen chloride or of benzene in the hydrochloride led to the isolation of *n*-butyl chloride (6·2 c.c. from 23 g. of hydrochloride in one experiment); the residual amines contained chiefly aniline, some *n*-butylaniline, and another primary amine in small quantity.

Rearrangement of Alkylanilines in Presence of Sulphates and Phosphates.

Silver Sulphate.—Ethylaniline (6 g.) and silver sulphate (2 g.), maintained at 200—230° for 16 hours, gave a dark brown, viscous mass having the odour of hydrogen sulphide and containing embedded in it a cake of silver sulphide with some silver sulphate (Found: Ag, 89·3; S, 6·4%). Extraction with alcohol, evaporation of the alcoholic solution with dilute hydrochloric acid, and filtration to remove tarry material yielded a solution from which *p*-aminoethylbenzene was isolated through its zincichloride and sulphate. Other primary amines, more complex than *p*-aminoethylbenzene, were also present, but were not isolated in a pure state.

Butylaniline, heated with silver sulphate under similar conditions, yielded *p*-amino-*n*-butylbenzene. A considerable proportion of more complex and amorphous products was present. The yield of pure sulphate was usually 0·2 g. from 5 g. of secondary amine. Prolonged heating reduced the yield of primary amine.

Anhydrous copper sulphate, heated with *n*-butylaniline at 200—250°, gave a dense black tar from which a primary amine was isolated as a sparingly soluble sulphate, but the yield was so small that the reaction was not further examined.

Copper Phosphate.—Ethylaniline (5 g.), heated with copper phosphate (2 g.) at 250° for 14 hours, yielded *p*-aminoethylbenzene, metallic copper (Cu, 98·6%), and metaphosphoric acid.

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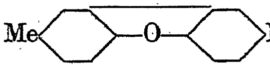
[*Received, June 15th,* 1926.]

XII.—*Substituted Diaryl Ethers. Part I. Di-*p*-tolyl Ether.*

By JOSEPH REILLY, PETER J. DRUMM, and HERBERT S. BOYD BARRETT.

WHILST the mixed ethers such as anisole and phenetole have been extensively studied, the substituted diaryl ethers derived from alkylphenols have received scarcely any attention, although from the newer aspects of chemical theory their reactions and the orientation of their derivatives are of interest.

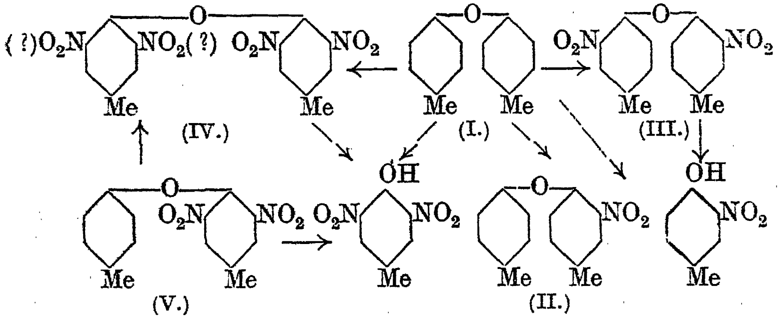
Di-*p*-tolyl ether was selected as typical of the class of substances indicated. The only two references to this compound in the literature are the following: Busch (*Ber.*, 1884, **17**, 2638) claimed to have prepared ditolyl ether by heating *p*-cresol with zinc chloride to 300° and gave the melting point as 165°, whilst Gladstone and Tribe (J., 1882, **41**, 9), by distilling aluminium *p*-tolyloxide, isolated, in small amounts, a substance of m. p. 50° which, from analogy with diphenyl ether, they called *p*-cresyl ether. In the present work, di-*p*-tolyl ether (I) was prepared in very good yield from *p*-cresol and *p*-bromotoluene, and the work of Gladstone and Tribe confirmed. Sabatier and Mailhe (*Compt. rend.*, 1910, **151**, 494), by the catalytic dehydration of *p*-cresol with thoria at 470°, obtained a compound similar to that of Busch to which they assigned the constitution 

, *i.e.*, di-*p*-tolylene ether. The present work supports the views of Sabatier and Mailhe. It would appear, therefore, that the only authentic reference in the literature to di-*p*-tolyl ether is that of Gladstone and Tribe (*loc. cit.*).

Di-*p*-tolyl ether behaves normally on oxidation, forming an ether acid which on distillation with soda-lime gives phenol and diphenyl ether.

Di-*p*-tolyl ether condenses with acetyl and benzoyl chlorides and phthalic anhydride in the presence of aluminium chloride to give monoketonic and not diketonic derivatives as might be expected. These develop characteristic colours with sulphuric acid, accompanied by fluorescence in the case of the last two compounds. These compounds behave abnormally with phenylhydrazine and hydroxylamine and will form the subject of a further communication.

The behaviour of di-*p*-tolyl ether on nitration is in many ways different from that of diphenyl ether and hitherto no nitration products of this substance have been described. Diphenyl ether nitrates smoothly to nitrodiphenyl ethers with very little decomposition to nitrophenols (Ryan and Drumm, *Proc. Roy. Soc. Dublin*, 1924, **17**, 313). Di-*p*-tolyl ether, on the other hand, under the different conditions of nitration described below, gave mono- and dinitro-*p*-cresols as the main product, the nature of the by-product, consisting of small quantities of various nitrodi-*p*-tolyl ethers, depending on the experimental conditions. Amongst the new nitro-products isolated and identified by synthesis were *2-nitrodi-*p*-tolyl ether* (II), *2 : 2'-dinitrodi-*p*-tolyl ether* (III), and a tetranitro-compound which is probably *2 : 6 : 2' : 6'-tetranitrodi-*p*-tolyl ether* (IV). 2 : 6-Dinitrodi-*p*-tolyl ether (V) was obtained by the condensation of *p*-cresol with 3 : 5-dinitro-*p*-bromotoluene. In addition, 3-nitro- and 3 : 5-dinitro-*p*-cresols were isolated in certain cases. The actual scheme of nitration may be indicated as follows:



2-Nitrodi-*p*-tolyl ether is readily reduced to 2-aminodi-*p*-tolyl ether, and the latter diazotises and gives azo-dyes. These substances, together with the amino-compounds from the other nitro-derivatives of di-*p*-tolyl ether, are being further examined.

EXPERIMENTAL.

Di-p-tolyl Ether.—In the preliminary experiments, *p*-cresol, *p*-bromotoluene, powdered potassium hydroxide, and a trace of copper bronze were heated at 200—250° for 3 to 4 hours, the procedure used in the case of diphenyl ether being followed. The product, on distillation in steam, gave much unchanged bromotoluene, followed by a small quantity of oil, which solidified (yield, 20—25%). By altering the method as follows, the yield was increased to 87%. Potassium *p*-tolyloxide (dried at 150° in a vacuum) (35 g.), *p*-bromotoluene (commercial *p*-bromotoluene purified by standing in contact with sulphuric acid to remove traces of isomerides; m. p. of purified product, 28·5°) (41 g.), copper bronze (Naturkupfer C; washed with ether to remove oily impurities) (0·3 g.), and *p*-cresol (20 g.) (solvent) were slowly heated in a dried flask fitted with an air condenser. Reaction commenced at 200°, with separation of potassium bromide. The heating was continued for 2 hours at 230—240°. The dark product was made alkaline with aqueous potassium hydroxide and distilled in steam. Unchanged bromotoluene passed over, followed by an oil which quickly solidified; this crystallised from ethyl alcohol in colourless prisms, m. p. 50° (Found: C, 84·5; H, 7·3; *M*, cryoscopic in naphthalene, 191. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%; *M*, 198).

Di-*p*-tolyl ether is very soluble in acetone, ether, or benzene, readily soluble in hot alcohol or warm glacial acetic acid, and insoluble in water. It has a pleasant odour, similar to, but fainter than, that of diphenyl ether.

Di-p-*tolylene Oxide.*—*p*-Cresol (25 g.) and litharge (50 g.) were intimately mixed and heated (oil-bath) at 110—120° for 10 hours. The product, after cooling, was powdered and distilled. At first, unchanged *p*-cresol passed over. The fraction, b. p. above 300°, set to a crystalline solid and separated from boiling light petroleum (b. p. 70—100°) in glistening, pearly plates, m. p. 165°. Prepared in a manner analogous to that of diphenylene oxide from phenol, this substance is obviously di-*p*-tolylene oxide. Its further investigation is in progress.

Oxidation of Di-p-*tolyl Ether.*—A solution of chromic acid in glacial acetic acid was gradually added, with stirring, to an acetic acid solution of di-*p*-tolyl ether at 40° until oxidation was apparently completed. The gelatinous precipitate that formed on dilution with water was separated from the liquid by the streamline filter, washed with water, and repeatedly dissolved in aqueous ammonia and precipitated with hydrochloric acid. The collected solid was converted into the silver salt in the usual manner (Found: Ag, 45·4. $C_{14}H_8O_5Ag_2$ requires Ag, 45·7%). Di-*p*-carboxydiphenyl ether is a white, amorphous solid which does not melt. It is easily soluble in alkalis and is precipitated therefrom by acids. The silver salt, sparingly soluble in water, is readily soluble in ammonia.

An intimate mixture of the above acid (1 part) with dry sodalime (4 parts) was strongly heated in a retort. The small amount of oil, smelling strongly of phenol, that distilled was extracted with ether, and the ethereal layer well washed with aqueous sodium hydroxide to remove phenolic substances. On evaporation of the ether an oil remained which gradually solidified in a freezing mixture. This substance, m. p. 28°, was identified as diphenyl ether by the method of mixed melting point.

Action of Nitric Acid on Di-p-*tolyl Ether under Various Conditions.*—*In acetic acid solution.* To a well-cooled solution of nitric acid (12 c.c.; *d* 1·5) in glacial acetic acid (50 c.c.), di-*p*-tolyl ether (5 g.) was slowly added, with constant stirring. The temperature was allowed to rise slowly to 30°, and the red solution was then poured on to crushed ice. The precipitated yellow oil in ethereal solution was washed with dilute potassium hydroxide solution and with water and dried. The residual oil, cooled in a freezing mixture, set to a crystalline solid (2 g.) which was dried on a porous tile and crystallised from ethyl alcohol, colourless prisms, m. p. 50°, being obtained (Found: N, 5·6. $C_{14}H_{13}O_3N$ requires N, 5·7%). This substance (A) is therefore one of the mononitro-derivatives of di-*p*-tolyl ether and its constitution was determined later by direct synthesis. The dark red potash extract was acidified with dilute hydrochloric acid, and the yellow precipitate collected and distilled in steam. From the distillate a yellow solid separated (1 g.). This, after crystallisation from dilute aqueous ethyl alcohol, melted at 33° and showed no depression of melting point when mixed with 3-nitro-*p*-cresol. From the residue after distillation was isolated a crystalline substance (2 g.), m. p. 85°, which was identified as 3 : 5-dinitro-*p*-cresol by the mixed melting-point method.

Direct nitration. Cold nitric acid of concentrations up to *d* 1·4 is without appreciable action on di-*p*-tolyl ether. On heating the mixture a very vigorous reaction, which was difficult to control, commenced at 70°, with copious evolution of nitrous fumes. With nitric acid of a higher density, under the following conditions, a dinitrodi-*p*-tolyl ether was isolated. Di-*p*-tolyl ether (5·5 g.) was added during 1 hour to nitric acid (10 c.c.; *d* 1·5) at —10° to —5°. In the absence of very efficient external cooling the reaction tends to become rather violent. The resulting dark red solution was poured on to crushed ice. The precipitated oily solid was washed in ethereal solution with dilute aqueous sodium hydroxide, until this showed no coloration, then with water, and dried. The residue from the ethereal solution was re-extracted with light petroleum (b. p. 70—100°). From the latter, a yellow substance (B) (1 g.) slowly separated which crystallised from alcohol in slender plates, m. p. 126° (Found: N, 9·9. $C_{14}H_{12}O_5N_2$ requires N, 9·7%). The constitution of this dinitrodi-*p*-tolyl ether was determined later by direct synthesis. From the alkaline extract 3 : 5-dinitro-*p*-cresol (4 g.) was isolated in the usual way.

With a mixture of sulphuric and nitric acids. Finely powdered di-*p*-tolyl ether (5 g.) was added slowly to a mixture of 98% sulphuric acid (25 g.) and nitric acid (25 g.; *d* 1·5) at —10° with thorough stirring and cooling in a freezing mixture. The resulting highly-coloured solution was poured on to crushed ice. The precipitated light brown oil was extracted with ether, and the ether extract freed from nitrocresols in the usual way. From the ether was obtained a yellow solid (1 g.) which was separated into two fractions by means of boiling light petroleum (b. p. 70—100°); the soluble part consisted of a dinitrodi-*p*-tolyl ether identical with that obtained by direct nitration; the insoluble portion (C) separated from boiling ethyl alcohol in colourless, rectangular plates, m. p. 246° (Found: N, 14·6. $C_{14}H_{10}O_9N_4$ requires N, 14·8%). This analysis agrees with that for a tetranitrodi-*p*-tolyl ether and the orientation of two of the nitro-groups has been ascertained as described later.

*Action of Gaseous Nitrogen Peroxide on Di-*p*-tolyl Ether.*—Dry liquid nitrogen peroxide, prepared from dry lead nitrate, and di-*p*-

tolyl ether were placed in two shallow containers left side by side under a bell-jar. Initially the absorption of the nitrogen peroxide was rapid and it needed renewal from time to time. The tolyl ether lost its crystalline form and after a week appeared as an intumescent, brown syrup. The method of working up employed was the same as that for the products of direct nitration. From it was isolated, in addition to 3:5-dinitro-*p*-cresol, a dinitrodi-*p*-tolyl ether (1·2 g.), m. p. 126°, identical in every respect with the dinitro-product obtained by direct nitration.

Syntheses of Nitrodi-p-*tolyl Ethers.*—2-*Nitrodi*-p-*tolyl ether*. Potassium *p*-tolyloxide (7 g., dried at 150° in a vacuum), 4-bromo-3-nitrotoluene (9 g.), copper bronze (0·1 g.), and *p*-cresol (20 g.) (solvent) were slowly heated (oil-bath), with stirring, in a flask fitted with an air condenser. At 160°, reaction set in with separation of potassium bromide. Heating was continued for 3 hours at 210—220°. The dark product was extracted with ether and the ethereal layer was washed with dilute sodium hydroxide solution until the latter was colourless, and then with water. On fractionation of the dried ethereal extract under diminished pressure, a pale yellow oil (3 g.) distilled at 220°/15 mm. The oil solidified to a mass of light yellow crystals, m. p. 46—48°, and separated from alcohol in colourless prisms, m. p. 50° (Found: N, 5·6. $C_{14}H_{13}O_3N$ requires N, 5·7%). 2-Nitrodi-*p*-tolyl ether is freely soluble in benzene, ether, or chloroform, and less soluble in light petroleum (b. p. 70—100°) or ethyl alcohol. It is not hydrolysed by boiling with potassium hydroxide solution (20%), as evidenced by the negligible amount of colour developed in solution after 10 hours. The nitro-group was reduced by tin and hydrochloric acid; the resulting amino-compound diazotised and then coupled with alkaline β-naphthol to give a scarlet azo-dye. 2-Nitrodi-*p*-tolyl ether agrees in every respect, including mixed melting point, with the mononitro-derivative (A) obtained by nitration, in acetic acid solution, of di-*p*-tolyl ether.

2:2′-*Dinitrodi*-p-*tolyl ether*. Potassium 3-nitro-*p*-tolyloxide (6 g., dried at 100° in a vacuum), 4-bromo-3-nitrotoluene (6 g., prepared by diazotisation in dilute sulphuric acid of 3-nitro-*p*-toluidine with subsequent conversion into the diazonium perbromide and decomposition of this with a small amount of absolute ethyl alcohol), 3-nitro-*p*-cresol (15 g.) (solvent) and copper bronze (0·2 g.) were heated (oil-bath), with stirring, very slowly to 190°, and then, after 1 hour, to 210° during 3 hours. The highly coloured product was powdered and repeatedly extracted with ether, and the ethereal layer was freed from nitrocresol in the usual way. The residue left after removal of the ether was extracted with boiling light petroleum

(b. p. 70—100°), from which a yellow, crystalline solid slowly separated. This solid crystallised from ethyl alcohol in pale yellow, slender laminæ, m. p. 126° (Found: N, 9·9. $C_{14}H_{12}O_5N_2$ requires N, 9·7%).

2 : 2′-Dinitrodi-*p*-tolyl ether is colourless when pure, but gradually assumes a yellow colour in contact with air. It is very soluble in ether or benzene and readily soluble in hot light petroleum (b. p. 70—100°) or hot ethyl alcohol. It is slowly hydrolysed by boiling potassium hydroxide solution (20%), more readily by alcoholic potassium hydroxide, with formation of 3-nitro-*p*-cresol. It is identical with the dinitro-derivative (B) obtained by direct nitration of di-*p*-tolyl ether.

2 : 6-*Dinitrodi*-p-*tolyl ether*. Potassium *p*-tolyloxide (6 g.) and 3 : 5-dinitro-*p*-bromotoluene (prepared by the method of Jackson and Ittner, *J. Amer. Chem. Soc.*, 1897, **19**, 7) (7·5 g.) were heated in alcoholic solution on the steam-bath for 4 hours. The solution became orange-coloured and potassium bromide separated almost immediately. The solution was filtered hot and, on cooling, deposited faintly yellow crystals, m. p. 98—100°. The pure substance was obtained from alcohol in colourless, slender prisms, m. p. 107° (Found: N, 9·9. $C_{14}H_{12}O_5N_2$ requires N, 9·7%).

2 : 6-Dinitrodi-*p*-tolyl ether is easily soluble in ether, chloroform, or acetone and sparingly soluble in cold ethyl alcohol or cold light petroleum. It is readily hydrolysed by boiling alcoholic potassium hydroxide with formation of *p*-cresol and 3 : 5-dinitro-*p*-cresol. In contact with air, it gradually assumes a yellow colour.

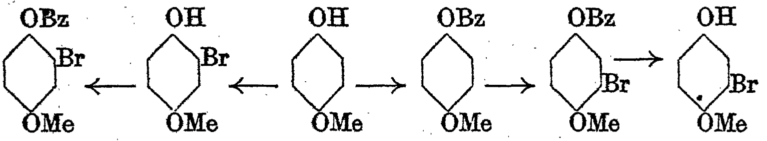
Nitration of 2 : 6-*Dinitrodi*-p-*tolyl Ether.*—To nitric acid (12 c.c.; *d* 1·5) was slowly added 2 : 6-dinitrodi-*p*-tolyl ether (2·6 g.), the temperature being maintained at −5°. The solution was then poured on to ice, and the yellow precipitate freed from small amounts of nitrocresols as before. The residue crystallised from glacial acetic acid in colourless plates, m. p. 246° (Found: N, 14·6. $C_{14}H_{10}O_9N_4$ requires N, 14·8%). The tetranitrodi-*p*-tolyl ether is freely soluble in acetone, much less soluble in ether, chloroform, or benzene, and practically insoluble in cold glacial acetic acid or light petroleum. It is readily hydrolysed by hot alcoholic potassium hydroxide with formation of 3 : 5-dinitro-*p*-cresol. It agrees in melting point and other properties with the tetranitro-compound (C) obtained by the nitration of di-*p*-tolyl ether in a mixture of nitric and sulphuric acids.

UNIVERSITY COLLEGE, CORK. [*Received, September 24th,* 1926.]

XIII.—*Bromination of Quinol Monomethyl Ether.*

By Frank Mouat Irvine and John Charles Smith.

Contrary to the statement by Kohn and Guttmann (*Monatsh.*, 1924, 45, 575) that dibromination of quinol monomethyl ether yields only the 2 : 5-dibromoquinol monomethyl ether, it has been proved that only 30—35% of this isomeride is formed, the main product being 2 : 6-dibromoquinol monomethyl ether, as would be expected. The monobromination also is normal. It has been shown that when quinol monomethyl ether (I) is first monobrominated and then benzoylated there is formed a different substance from that obtained when it is first benzoylated and then monobrominated, and that the unbenzoylated bromoquinol monomethyl ethers are different. As the relative directive powers of the hydroxy-, methoxy-, and benzoyloxy-groups are in the order OH > OMe > OBz, these two bromophenols must be 2-*bromoquinol monomethyl ether* (II) and 3-*bromoquinol monomethyl ether* (VI), and the corresponding benzoyl derivatives must be represented by (III) and (V), respectively.



(III.) (II.) (I.) (IV.) (V.) (VI.)

Experimental.

2-*Bromoquinol Monomethyl Ether* (II).—Quinol monomethyl ether (m. p. 53°, entirely free from quinol; compare Robinson and Smith, J., 1926, 393) gave a homogeneous monobromination product on treatment with excess of bromine in carbon disulphide solution.

To a solution of the quinol monomethyl ether (6·2 g.; 1 mol.) in cold carbon disulphide (140 c.c.) was slowly added, with stirring, a 20% (vol.) solution of bromine in carbon disulphide (12·5 c.c.; 1 mol.). When the yellow colour had almost disappeared, the solvent was distilled off. The residue, which solidified (m. p. 40—42°; yield, almost theoretical), was quickly recrystallised from ligroin (b. p. 60—80°) and obtained as long, colourless needles, m. p. 44—45° (Found: C, 41·5; H, 3·6. $C_7H_7O_2Br$ requires C, 41·4; H, 3·5%). The acetyl derivative was a liquid, but the *benzoyl* derivative (III), obtained in 95% yield by the Schotten-Baumann method, when recrystallised from ligroin (b. p. 80—100°), melted sharply at 85°

(Found: C, 54·8; H, 3·6; Br, 26·0. $C_{14}H_{11}O_3Br$ requires C, 54·7; H, 3·6; Br, 26·0%).

3-*Bromoquinol Monomethyl Ether* (VI).—4-*Methoxyphenyl benzoate* (IV), obtained by the Schotten-Baumann method, melted sharply at 87°, but required recrystallisation from alcohol and from ligroin before it was pure enough for analysis (Found: C, 73·6; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%). It could be brominated in warm acetic acid solution with an iron catalyst, or in anhydrous formic acid. The solid (11·4 g.; 1 mol.), dissolved in formic acid (75 c.c.), was warmed on a steam-bath while a solution of bromine (3·0 c.c.; 1·2 mols.) in an equal volume of formic acid was run in dropwise; the mixture was gently boiled for a few minutes until the excess of bromine was driven off, then poured into water (500 c.c.); the brown oil which formed rapidly solidified (16·1 g.). On recrystallisation from alcohol, pure 3-*bromo*-4-*methoxyphenyl benzoate* (V), white needles, m. p. 105·5°, was obtained (Found: C, 54·8; H, 3·6. $C_{14}H_{11}O_3Br$ requires C, 54·7; H, 3·6%). After hydrolysis with aqueous methyl-alcoholic sodium hydroxide, pure benzoic acid and a bromophenol (theoretical yields) were separated by means of sodium bicarbonate solution. Recrystallisation from a small volume of benzene gave long prisms, m. p. 77—78°, of 3-*bromoquinol monomethyl ether* (VI) (Found: C, 41·2; H, 3·5; Br, 39·5. $C_7H_7O_2Br$ requires C, 41·4; H, 3·5; Br, 39·4%).

2 : 6-*Dibromoquinol Dimethyl Ether*.—In the method of preparation given by Kohn and Guttmann (*loc. cit.*, p. 582), the following improvements were introduced. Tribromophenol bromide (m. p. 137—141°), obtained from phenol (1 g. in 750 c.c. of water) and excess of bromine water, was recrystallised from warm (40°) chloroform and found always to melt at 140—141° (decomp.) [Found: Br (by potassium iodide), 38·7. Calc.: Br, 39·0%]. It was found unnecessary to extract the crude tribromophenol bromide with alkali as recommended by Auwers and Büttner (*Annalen*, 1898, **302**, 141). 2 : 6-Dibromobenzoquinone (m. p. 132°), prepared from tribromophenol bromide and fuming nitric acid, was reduced in aqueous suspension by means of sulphur dioxide to 2 : 6-dibromoquinol; a quantitative yield was obtained by carrying out the reduction in the cold until the red colour first produced had almost disappeared (10 minutes) and then gradually warming the mixture to 100°. Methylations of 2 : 6-dibromoquinol (m. p. 162—163°) with sodium or potassium hydroxide solution and pure methyl sulphate gave crude products, m. p. 37—38° (yields, 70—85%); these, after recrystallisation from methyl or ethyl alcohol, formed almost regular hexagonal plates, m. p. 38—39°. Some days later, the crystals had changed to elongated hexagonal plates, the m. p.,

53°, of which was unaltered by further recrystallisation (Found: C, 32·3; H, 2·7; Br, 53·8. Calc.: C, 32·4; H, 2·7; Br, 54·0%). The crystals melting at 53° are exactly like those described and measured by Kohn and Guttmann but stated by them to melt at 56°.

Dibromination of Quinol Monomethyl Ether.—In every case, the dibromination of the quinol monomethyl ether (6·2 g.; 1 mol.) was performed at 10° in well-stirred glacial acetic acid solution (30 c.c.) by slowly adding bromine (5 c.c.; 2 mols.) in acetic acid (15 c.c.). A clean product * was obtained by distilling the hydrobromic and acetic acids during ¾ hour at 30—40°/5—10 mm. in a slow current of dry air drawn through the liquid. The residue (14·0 g.; quantitative yield) soon set to a pink, crystalline mass, m. p. 60—80°. It could be recrystallised from dilute acetic acid or from hexane; but the best method of separation was that of Kohn and Guttmann, by methylation, 2 : 5-dibromoquinol dimethyl ether (Habermann, *Ber.*, 1878, **11**, 1034) being insoluble in cold alcohol. Kohn and Guttmann, however, failed to realise that the easily soluble 2 : 6-dibromoquinol dimethyl ether might be present in the alcoholic mother-liquor.

In a test experiment, a mixture of 2 : 5-dibromoquinol dimethyl ether (m. p. 144—145°; 1·0 g.) and the 2 : 6-isomeride (1·0 g.) was recrystallised from alcohol and gave a first crop of 0·94 g., m. p. 142—143°. Complete evaporation of the mother-liquor left 1·02 g. of crystals, m. p. 45—48°, from which by repeated recrystallisation 0·2 g. of the pure 2 : 6-isomeride, m. p. 53°, was obtained. When 1·0 g. of the soft, colourless, crystalline mixture (m. p. 43—130°) from the methylation of some dibromination product (recrystallised from hexane) was recrystallised from alcohol, only 0·4 g. of 2 : 5-dibromoquinol dimethyl ether (m. p. 142—143·5°) was obtained. After complete evaporation of the mother-liquor, clusters of well-formed, elongated hexagonal plates (0·55 g.) remained, m. p. 45—50°. Repeated crystallisation from alcohol raised the m. p. to 51—53° (Found: Br, 53·9. Calc.: Br, 54·0%). The mixed melting point with a specimen of 2 : 6-dibromoquinol dimethyl ether, m. p. 53°, was 52—53°.

In order to obtain a more accurate analysis, experiments were performed in which the entire yields of the crude bromination products were methylated, and the dimethyl ethers isolated by extraction with ether. Losses in methylation would probably be heavier in the case of the diortho-substituted 2 : 6-isomeride, so that the proportion of 2 : 5-dibrominated product found would be a maximum. It is possible also that some 2 : 3-dibromoquinol dimethyl ether (a compound not yet known) was formed. In two experiments, 6·2 g. of quinol monomethyl ether gave 12·85 g. (yield, 87%) and 11·70 g. (yield, 79%), respectively, of mixed dibromoquinol dimethyl ethers; the quantities of the 2 : 5-isomeride isolated were 4·30 g. (yield, 33·5%) and 3·65 g. (yield, 31·2%), respectively.

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* The addition of ice-water to the stirred reaction mixture at first precipitates a cream-coloured oil, but the colour suddenly turns reddish-brown and then black, large amounts of tar being formed.

Summary.

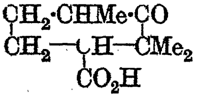
Quinol monomethyl ether yields on monobromination 2-*bromoquinol monomethyl ether*, and on dibromination not more than 30—35% of 2 : 5-dibromoquinol monomethyl ether, the remainder being mostly 2 : 6-dibromoquinol monomethyl ether. 3-*Bromoquinol monomethyl ether* also is described.

THE UNIVERSITY, MANCHESTER. [*Received, November 6th,* 1926.]

XIV.—*The Constitution of the Acid formed by the Action of Sulphuric Acid on Camphorquinone.*

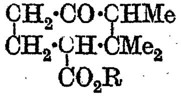
By MADHAV BALAJI BHAGVAT and JOHN LIONEL SIMONSEN.

IN a recent communication (J., 1925, **127**, 1294), evidence was advanced which appeared to prove that the keto-acid, $C_{10}H_{16}O_3$, first prepared by Manasse and Samuel (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831) by the action of sulphuric acid on camphorquinone, was *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid (I). The assignment of this constitution to the acid was based essentially on two facts: (i) on oxidation with nitric acid it gave β-methylpentane-βγε-tricarboxylic acid (III), and (ii) on treatment with amyl nitrite and hydrochloric acid it did not yield an oximino-derivative, the formation of which might have been expected if the keto-acid had the alternative constitution (II) (compare footnote, *loc. cit.*, p. 1295), since in this case there is a methylene group adjacent to the carbonyl group.



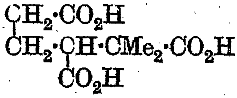
$$\begin{array}{l} CH_2\cdot CHMe\cdot CO \\ CH_2—CH—CMe_2 \\ \qquad CO_2H \end{array}$$

(I.)



$$\begin{array}{l} CH_2\cdot CO\cdot CHMe \\ CH_2\cdot CH\cdot CMe_2 \\ \qquad CO_2R \end{array}$$

(II.; R = H, Me.)

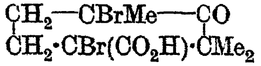


$$\begin{array}{l} CH_2\cdot CO_2H \\ CH_2\cdot CH\cdot CMe_2\cdot CO_2H \\ \qquad CO_2H \end{array}$$

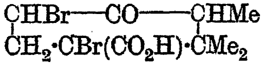
(III.)

In deciding between these two formulæ, owing to the symmetry of the molecules, simple degradation products were unlikely to be of much assistance, but it seemed probable that, on bromination, a dibromo-acid would result of either formula (IV) or (V). It was further anticipated that this acid would, on removal of two molecules of hydrogen bromide, tend to lose simultaneously a methyl group and so pass into a phenolic acid (VI or VII) the identification of which would have offered little difficulty.

(IV.)



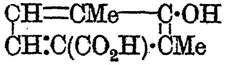
$$\begin{array}{l}CH_2\text{—}CBrMe\text{—}CO\\ CH_2\cdot CBr(CO_2H)\cdot CMe_2\end{array}$$



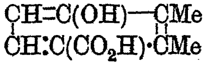
$$\begin{array}{l}CHBr\text{—}CO\text{—}CHMe\\ CH_2\cdot CBr(CO_2H)\cdot CMe_2\end{array}$$

(V.)

(VI.)



$$\begin{array}{l}CH{=}CMe\text{—}C\cdot OH\\ CH{:}C(CO_2H)\cdot CMe\end{array}$$



$$\begin{array}{l}CH{=}C(OH)\text{—}CMe\\ CH{:}C(CO_2H)\cdot CMe\end{array}$$

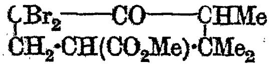
(VII.)

On bromination in acetic acid, the crystalline and the liquid methyl ester of the keto-acid each gave a *dibromo*-ester, $C_{11}H_{16}O_3Br_2$, which reacted in an identical manner with alkali. In some experiments, under conditions which could not be exactly defined, the dibromo-ester was obtained crystalline. Since both the pure crystalline ester and the crude liquid ester yielded the same products, they were apparently stereoisomerides.

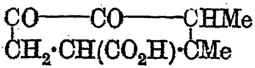
On treatment with a solution of barium or potassium hydroxide the dibromo-ester gave a complex mixture of acids, from which, with considerable difficulty, (A) a *hydroxyketo-acid*, $C_{10}H_{14}O_4$, m. p. 151—152°, (B) a dibasic *hydroxy-acid*, $C_{10}H_{16}O_5$, m. p. 191—192°, (C) and (D) unsaturated dibasic *acids*, $C_{10}H_{14}O_4$, m. p. 257° and 215—216°, respectively, were isolated.

The formation of the hydroxyketo-acid, which also reacted as a diketo-acid, yielding a *dioxime* and a *disemicarbazone*, would appear to indicate that the dibromo-ester has two bromine atoms attached to the same carbon atom—a fact most simply explained if the original keto-ester has formula (II), the dibromo-ester then being represented by (VIII). An ester of this formula should yield on treatment with alkali a diketo-acid (IX); the acid obtained, however, and also its *methyl* ester, were colourless substances which gave intense colorations with ferric chloride, and the methyl ester was readily soluble in dilute potassium hydroxide solution and reprecipitated by carbon dioxide. Moreover, in alkaline solution, the acid was unstable to potassium permanganate and on treatment with acetyl chloride it yielded an *acetyl* derivative. There can be no doubt, therefore, that the hydroxyketo-acid is represented by (X) or (XI), the latter being the more probable, since the acid shows no tendency to yield a lactone. Owing to the small quantity of material available, the decision between these two formulæ could not be made.

(VIII.)



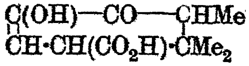
$$\begin{array}{l}CBr_2\text{—}CO\text{—}CHMe\\ CH_2\cdot CH(CO_2Me)\cdot CMe_2\end{array}$$



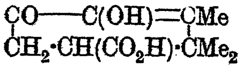
$$\begin{array}{l}CO\text{—}CO\text{—}CHMe\\ CH_2\cdot CH(CO_2H)\cdot CMe\end{array}$$

(IX.)

(X.)



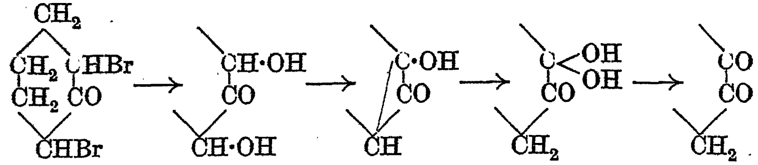
$$\begin{array}{l}C(OH)\text{—}CO\text{—}CHMe\\ CH\cdot CH(CO_2H)\cdot CMe_2\end{array}$$



$$\begin{array}{l}CO\text{—}C(OH){=}CMe\\ CH_2\cdot CH(CO_2H)\cdot CMe_2\end{array}$$

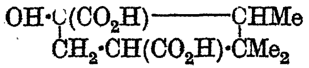
(XI.)

In its general properties this acid resembles the diketones or, more correctly, the hydroxy-ketones obtained by Wallach (*Annalen*, 1918, 414, 296) in an analogous manner by the action of alkali on the dibromo-derivatives of various cyclic ketones. Wallach considered that the two bromine atoms were not attached to the same carbon atom and that the formation of the diketone proceeded in accordance with the scheme :



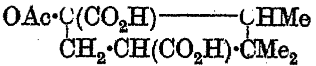
Our experiments do not furnish any evidence in support of this somewhat complicated series of reactions and we prefer for the present to assume that the dibromo-ester has formula (VIII).

The hydroxyketo-ester (or acid), on digestion with a strong solution of potassium hydroxide (50% KOH), behaves in a similar manner to Wallach's hydroxy-ketones, undergoing molecular rearrangement with addition of water and becoming converted into a dibasic hydroxy-acid identical with the acid (B) that forms the main product of the action of alkali on the dibromo-ester. There can be no doubt that this acid is 1-*hydroxy*-4 : 4 : 5-*trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (XII). It yields an unsaturated acid when heated above its melting point and gives an *acetyl* derivative (XIII) when digested with acetic anhydride. It is somewhat remarkable that the acid yields neither a lactone nor an anhydride,



$$\begin{array}{l} OH\cdot C(CO_2H)\text{———}CHMe \\ \quad CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$$

(XII.)

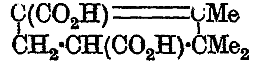


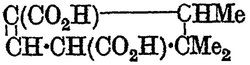
$$\begin{array}{l} OAc\cdot C(CO_2H)\text{———}CHMe \\ \quad CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$$

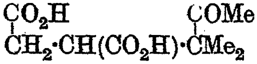
(XIII.)

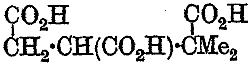
since either the carboxyl groups or the hydroxyl and one carboxyl group must be in the *cis*-position. We are of opinion that the carboxyl groups are in the *trans*-position, because the acetyl derivative of the hydroxy-acid, when heated to its melting point, loses acetic acid and is converted quantitatively into an unsaturated acid, $C_{10}H_{14}O_4$, m. p. 257°. This acid is identical with the unsaturated acid (C) referred to on p. 78 and must be represented by formula (XIV) or (XV); there can be no doubt that it is 4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* (XIV). On oxidation with potassium permanganate, it yields a dibasic *keto-acid*, $C_9H_{14}O_5$, m. p. 125—126°, which, on further oxidation with sodium hypobromite, gives γ-methylbutane-αβγ-tricarboxylic acid (XVIII). The keto-acid must therefore be *γ-acetyl-γ-methylbutane-αβ-di-*

carboxylic acid (XVII). γ-Methylbutane-$\alpha\beta\gamma$-tricarboxylic acid is also formed when 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid is oxidised with dilute nitric acid.

(XIV.)

$$\begin{array}{l}\mathrm{C(CO_2H){=\!=}CMe}\\ \mathrm{CH_2{\cdot}CH(CO_2H){\cdot}CMe_2}\end{array}$$


$$\begin{array}{l}\mathrm{C(CO_2H){-\!-}CHMe}\\ \mathrm{CH{\cdot}CH(CO_2H){\cdot}CMe_2}\end{array}$$
(XV.)

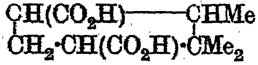
(XVII.)

$$\begin{array}{l}\mathrm{CO_2H \qquad\quad COMe}\\ \mathrm{CH_2{\cdot}CH(CO_2H){\cdot}CMe_2}\end{array}$$

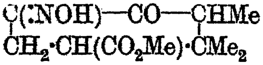

$$\begin{array}{l}\mathrm{CO_2H \qquad\quad CO_2H}\\ \mathrm{CH_2{\cdot}CH(CO_2H){\cdot}CMe_2}\end{array}$$
(XVIII.)

When 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid is oxidised with potassium permanganate at 0°, in addition to γ-acetyl-γ-methylbutane-$\alpha\beta$-dicarboxylic acid a second *keto-dicarboxylic acid*, $C_{10}H_{12}O_5$, m. p. 183—185°, is formed. This acid, which was characterised by the preparation of the *oxime* and *semicarbazone*, was unstable to potassium permanganate in alkaline solution. It was unfortunately not obtained in quantity and we are unable to suggest a satisfactory formula or account for its formation. The reaction would appear to be abnormal and recalls the conversion of Δ^1-*cyclo*hexeneacetic acid into 1-acetyl-Δ^1-*cyclo*pentene by an alkaline solution of potassium permanganate (Perkin and Wallach, *Ber.*, 1909, 42, 145). On oxidation with dilute nitric acid, the keto-acid yielded γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid, whilst on treatment with sodium hypobromite solution, although carbon tetrabromide and bromoform separated, the product was a resin which could not be crystallised and contained an appreciable quantity of bromine.

4 : 4 : 5-Trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid was somewhat resistant to reducing agents, but it was converted into the saturated *cyclo*pentane *acid* (XVI) by an excess of sodium and boiling amyl alcohol.

Unlike all the substances so far described, the unsaturated acid (D), m. p. 215—216° (p. 78) was optically active, the *sodium* salt being lævorotatory. Since the acid was racemised, with formation of the saturated cyclic acid (XVI), on reduction with sodium and amyl alcohol and yielded γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid on oxidation with nitric acid, there can be no doubt that it is the lævo-form of (XIV).

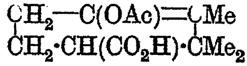
(XVI.)

$$\begin{array}{l}\mathrm{CH(CO_2H){-\!-}CHMe}\\ \mathrm{CH_2{\cdot}CH(CO_2H){\cdot}CMe_2}\end{array}$$


$$\begin{array}{l}\mathrm{C(:NOH){-}CO{-}CHMe}\\ \mathrm{CH_2{\cdot}CH(CO_2Me){\cdot}CMe_2}\end{array}$$
(XIX.)

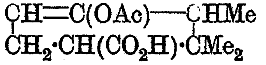
The foregoing results appear to us to establish definitely that the keto-acid first described by Manasse and Samuel must be d-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylic acid* (II), and it became necessary once more to attempt the preparation of an oximino-derivative. Although neither the acid nor the methyl ester could be induced to react with benzaldehyde or piperonal, the methyl ester reacted with amyl nitrite in the presence of sodium to yield an oil which was soluble in alkali and was evidently the crude *oximino-ester* (XIX). This ester could not be obtained crystalline, but on hydrolysis with formaldehyde and hydrochloric acid, followed by treatment with a dilute solution of potassium hydroxide, it gave an acid which partly crystallised on keeping. This acid, which was evidently somewhat impure 4-hydroxy-2 : 2 : 3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylic acid (XI), was not purified, but was converted into the *cyclo*pentene acid by the reactions outlined above. The acid melted at 257° and was identical with that prepared from the dibromo-ester. The formation of 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid in this manner would appear to eliminate definitely any possibility of molecular rearrangement during its formation from the bromo-ester.

The suggestion (*loc. cit.*, p. 1296) that the keto-acid can exist in keto- and enol forms has been confirmed by Mr. Aswath Narain Rao, who has prepared the *acetyl* derivative of the enolic form by treating camphorquinone with acetic anhydride and zinc chloride. This acetyl derivative is lævorotatory in chloroform solution and does not show mutarotation. It may be represented by formula (XX) or (XXI), and from analogy with the other unsaturated acids here referred to we are inclined to consider (XX) the more probable.

(XX.)



$$\begin{array}{l} CH_2—C(OAc)=CMe \\ | \qquad\qquad\qquad\qquad | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$$

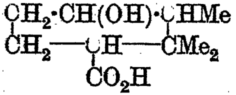


$$\begin{array}{l} CH=C(OAc)—CHMe \\ | \qquad\qquad\qquad\qquad | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$$

(XXI.)

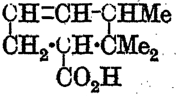
On hydrolysis, the acetyl derivative yields the ordinary ketonic form of the acid and all attempts to prepare it by direct acetylation have proved unsuccessful.

Since the acid previously considered to be *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid has now been shown to be *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid, the constitution of some of the compounds prepared from it require revision. *trans-d*-3-Hydroxy-2 : 2 : 4-trimethyl*cyclo*hexane-1-carboxylic acid should be *trans-d*-4-hydroxy-2 : 2 : 3-trimethyl*cyclo*hexane-1-carboxylic acid (XXII), and the unsaturated acid derived therefrom must be represented by formula (XXIII) or (XXIV).



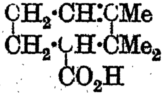
$$\begin{array}{l} CH_2\cdot CH(OH)\cdot CHMe \\ | \qquad\qquad\qquad\quad | \\ CH_2—CH—CMe_2 \\ \qquad\quad | \\ \qquad CO_2H \end{array}$$

(XXII.)



$$\begin{array}{l} CH=CH-CHMe \\ | \qquad\qquad\quad | \\ CH_2\cdot CH\cdot CMe_2 \\ \qquad\ | \\ \quad CO_2H \end{array}$$

(XXIII.)



$$\begin{array}{l} CH_2\cdot CH:CMe \\ | \qquad\qquad\ | \\ CH_2\cdot CH\cdot CMe_2 \\ \qquad\ | \\ \quad CO_2H \end{array}$$

(XXIV.)

EXPERIMENTAL.

Bromination of Methyl 2 : 2 : 3-*Trimethyl*cyclo*hexan*-4-*one*-1-*carboxylate. Methyl* 5 : 5-*Dibromo*-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-

carboxylate (VIII).—To a well-cooled solution of the crystalline methyl ester (55 g.) in acetic acid (280 c.c.), bromine (91·4 g.), dissolved in acetic acid (91·4 c.c.), was added. The reaction mixture was poured on to ice and the viscid oil which separated was washed with dilute aqueous sodium carbonate solution and dried in ethereal solution. On evaporation of the ether, the *dibromo-ester* was usually obtained as a brown oil, but in one experiment this gradually crystallised in needles; these were collected, drained on porous porcelain, and recrystallised from methyl alcohol, the dibromo-ester thus being obtained in glistening prisms, m. p. 57—58° (Found : Br, 45·1. $C_{11}H_{16}O_3Br_2$ requires Br, 44·9%).

Action of Barium Hydroxide on Methyl 5 : 5-*Dibromo*-2 : 2 : 3-*trimethyl*cyclo*hexan*-4-*one*-1-*carboxylate.*—A mixture of the crystalline (or liquid) dibromo-ester (26 g.) with a hot solution of barium hydroxide (52 g. in 170 c.c. of water) was boiled with constant agitation during 1 hour. The hot solution was filtered from a little insoluble matter (from which a further quantity of the mixed acids was obtained after treatment with a boiling solution of potassium hydroxide) and acidified. The liberated acids, which were isolated as a viscid brown oil (15 g.) by means of ether and partly crystallised on keeping, were esterified with methyl alcohol in the usual manner, and the esters formed were dissolved in ether. The ethereal solution was washed with dilute aqueous sodium carbonate (A), and then with 5% sodium hydroxide solution (B) until a test portion no longer gave a colour with ferric chloride. The ethereal solution was then dried and the solvent evaporated (C).

The sodium carbonate extract (A) on acidification yielded a small quantity of a resinous acid which was not further examined.

Methyl 4-*Hydroxy*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexen*-5-*one*-1-*carboxylate* (formula as XI).—The deep red sodium hydroxide extract (B) was saturated with carbon dioxide and the colourless crystalline solid that separated was collected (1·4 g.); the alkaline solution was then acidified and the viscid red oil produced was added to the mixture of acids obtained in later experiments and re-esterified.

The crystalline solid separated from light petroleum in rosettes of prismatic needles, m. p. 73—74° (Found: C, 61·9; H, 7·6. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%). The ester was appreciably soluble in hot water and dissolved readily in all the ordinary organic solvents except light petroleum, in which it was somewhat sparingly soluble. It gave with alcoholic ferric chloride a dirty green coloration, which was discharged by a trace of alkali.

The *dioxime*, which was obtained by heating the ester with hydroxylamine hydrochloride and sodium acetate in methyl-alcoholic solution, crystallised from benzene in fine needles, m. p.

138—139° (Found: C, 54·1; H, 7·5; N, 11·9. $C_{11}H_{18}O_4N_2$ requires C, 54·5; H, 7·4; N, 11·6%). In alcoholic solution it gave with ferric chloride a deep brown coloration. The *disemicarbazone* separated from hot water, in which it was somewhat readily soluble, in prisms, m. p. 206—207° (Found: N, 25·9. $C_{13}H_{22}O_4N_6$ requires N, 25·8%).

4-Hydroxy-2:2:3-trimethyl-Δ^3-cyclo*hexen-5-one-1-carboxylic acid* (XI), obtained by hydrolysing the methyl ester on the water-bath with a slight excess of dilute potassium hydroxide solution, crystallised from hot water or toluene in prismatic needles, m. p. 151—152° (Found: C, 60·8, 60·7; H, 7·4, 7·2. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). It was readily soluble in hot water, alcohol, acetone, or ether, but more sparingly soluble in chloroform, benzene, or toluene, and gave a dirty bluish-green coloration with aqueous or alcoholic ferric chloride. In alkaline solution it immediately decolorised potassium permanganate, but it did not react with bromine. The acid was readily oxidised by hydrogen peroxide, but the crystalline products were too small in quantity for identification. It condensed with *o*-phenylenediamine, and on treatment with phenylhydrazine it gave a mixture of the *mono-* and the *di-phenylhydrazone* as a yellow, amorphous solid, which was purified by solution in alkali and precipitation by acid (Found: N, 11·5. $C_{16}H_{20}O_3N_2$ requires N, 9·7%. $C_{22}H_{26}O_2N_4$ requires N, 14·8%).

The *acetyl* derivative, prepared by digesting the acid with acetyl chloride, crystallised from water in irregular plates; these melted at 95° when air-dried and at 128° after being dried over sulphuric acid. They retained water of crystallisation (½ mol.) even after being kept for some months in a vacuum over phosphoric oxide (Found: C, 58·0; H, 6·7. $C_{12}H_{16}O_5,\frac{1}{2}H_2O$ requires C, 57·8; H, 6·8%).

Conversion of 4-Hydroxy-2 : 2 : 3-trimethyl-Δ^3-cyclo*hexen-5-one-1-carboxylic Acid into 1-Hydroxy-4 : 4 : 5-trimethyl*cyclo*pentane-1 : 3-dicarboxylic Acid* (XII).—A mixture of the hydroxyketo-acid (1 mol.) and 50% potassium hydroxide solution (3 mols.) was boiled for 1 hour. The product, obtained in quantitative yield on cooling and acidification, melted at 191—192° after crystallisation from hot water and was identified with the following acid by the mixed melting-point method (Found: C, 55·1; H, 7·9%).

*1-Hydroxy-4 : 4 : 5-trimethyl*cyclo*pentane-1 : 3-dicarboxylic Acid* (XII).—The ester fraction (C) (p. 82) distilled almost entirely at 150—160°/10 mm. as a colourless oil, which was a mixture. The ester from one experiment (55 g.) was heated with an excess of methyl-alcoholic potassium hydroxide on the water-bath for 1 hour, and the solution kept at 0° for 12 hours. A somewhat sparingly soluble *potassium* salt separated in needles. This was well washed with ice-cold methyl alcohol (the filtrate, C_1, was reserved for later examination), dissolved in the minimum quantity of water, and acidified; a precipitate (16 g.) separated, and a little more was extracted from the filtrate with ether. 1-*Hydroxy*-4 : 4 : 5-*tri-methyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* thus obtained crystallised from hot water in glistening needles, m. p. 191—192° after softening at 184°, which contained $\frac{1}{2}H_2O$ (Found : C, 53·2; H, 7·8; H_2O, 4·0. $C_{10}H_{16}O_5,\frac{1}{2}H_2O$ requires C, 53·3; H, 7·6; H_2O, 4·0%. Found in material dried at 110° : C, 55·5; H, 7·5. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·4%). It was sparingly soluble in benzene, chloroform, or light petroleum, readily soluble in alcohol or acetic acid, gave no coloration with ferric chloride, was stable to potassium permanganate in alkaline solution, and was optically inactive.

The acid was treated with phosphorus pentachloride (3 mols.), and the product, after removal of the phosphorus oxychloride under diminished pressure, poured into formic acid. 4 : 4 : 5-Trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid, m. p. 257°, was thus obtained in poor yield; the other products of the reaction were not examined.

The *acetyl* derivative (XIII) formed when the hydroxy-acid was digested for 1 hour with an excess of acetic anhydride was obtained in needles on addition of water and concentration of the solution; it was recrystallised from hot water, in which it was somewhat sparingly soluble (Found : C, 55·7; H, 7·5. $C_{12}H_{18}O_6$ requires C, 55·8; H, 7·0%). It decomposed at 207—208° and immediately resolidified to a product, m. p. 257°, which was 4 : 4 : 5-trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid; the elimination of acetic acid is quantitative and this is the simplest method for the preparation of the pure unsaturated acid.

4 : 4 : 5-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic Acid* (XIV).—The methyl-alcoholic solution (C_1, above) from which the potassium salt of the hydroxy-acid had been separated was freed from alcohol on the water-bath and acidified; the crystalline precipitate was collected (7 g.) and the filtrate (C_2) reserved. By recrystallising the former from methyl alcohol, 4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* was obtained in glistening rhombohedra, m. p. 257—258° (Found : C, 60·5; H, 7·2; *M*, 197·8. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; *M*, 198). It was very sparingly soluble in water, ether, benzene, or chloroform, and more readily soluble in hot methyl alcohol, acetic acid, or formic acid. It immediately decolorised an alkaline solution of potassium permanganate, but reacted neither with bromine in acetic acid solution nor with sodium amalgam at the ordinary temperature. When heated above its

melting point, it did not yield an anhydride, but sublimed in long needles with very little decomposition. The aqueous solution of the *sodium* salt was optically inactive. The *dianilide*, prepared from the acid chloride in the usual manner, crystallised from dilute alcohol in fine needles, m. p. 200—201° (Found : C, 75·7 ; H, 7·4. $C_{22}H_{24}O_{22}N_2$ requires C, 75·9 ; H, 6·9%).

4 : 4 : 5-*Trimethyl*cyclo*pentane*-1 : 3-*dicarboxylic acid* (XVI) was obtained in an excellent yield when the unsaturated acid was reduced with sodium and amyl alcohol. It separated from hot water in soft, glistening prisms, m. p. 182—183°, and showed no tendency to yield an anhydride, small quantities distilling unchanged. It would appear, therefore, to be the *trans*-acid. It was readily soluble in hot water, alcohol, or ethyl acetate, and very sparingly soluble in benzene or chloroform (Found: C, 59·7; H, 8·3. $C_{10}H_{16}O_4$ requires C, 60·0 ; H, 8·0%).

1-4 : 4 : 5-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic Acid.*—The filtrate (C_2), on extraction with ether, yielded a viscid yellow oil which could not be purified. Since it apparently contained a quantity of the hydroxy*cyclo*pentanedicarboxylic acid, it was digested with acetic anhydride and the crude acetyl derivative was heated at 200—210° until all evolution of acetic acid had ceased. The melt was dissolved in sodium carbonate solution, filtered from a little tar, and acidified. The solid which separated was collected, the filtrate (C_3) being reserved, and recrystallised from methyl alcohol, a further quantity of the *cyclo*pentene acid, m. p. 257°, being obtained. The methyl-alcoholic filtrate was evaporated, and the residue repeatedly crystallised from formic acid; 1-4 : 4 : 5-*trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic acid* was thus obtained in irregular plates, m. p. 215—216° (Found : C, 60·5; H, 7·5. $C_{10}H_{14}O_4$ requires C, 60·6 ; H, 7·1%). This acid was very much more readily soluble in all the ordinary organic solvents than its inactive isomeride. On reduction with sodium and amyl alcohol, it yielded the inactive *cyclo*pentane acid (XVI). Under the conditions used for the oxidation of the racemic acid with nitric acid (see below), it gave γ-methylbutane-$\alpha\beta\gamma$-tricarboxylic acid, decomp. 154—155°, thus leaving no doubt as to its constitution. The sodium salt was lævorotatory in aqueous solution; $[\alpha]_D^{25^\circ}$ −62°.

The *dianilide* crystallised from dilute alcohol in glistening cubes, m. p. 208—209° (Found : N, 8·4. $C_{22}H_{24}O_2N_2$ requires N, 8·0%).

The filtrate (C_3, above) gave on extraction with ether a viscid oil which on trituration with formic acid yielded a further small quantity of the *l*-unsaturated acid. The formic acid mother-liquor contained an oil which was not examined.

Oxidation of 4 : 4 : 5-*Trimethyl*-Δ^5-cyclo*pentene*-1 : 3-*dicarboxylic Acid.*—(i) *With nitric acid.* The unsaturated acid (2 g.) was heated with nitric acid (*d* 1·2 ; 35 c.c.) on a water-bath for 8 hours and on a sand-bath for 8 hours; nitric acid (*d* 1·4; 15 c.c.) was then added, and the heating continued for a further 8 hours, a clear solution being obtained. The excess of mineral acid was removed on the water-bath; the viscid oily residue, on trituration with a little hydrochloric acid, crystallised almost completely. After draining on porous porcelain, it was recrystallised from a little hydrochloric acid, γ-methylbutane-αβγ-tricarboxylic acid separating in rosettes of needles, decomp. 154—155° (Found : C, 47·2; H, 5·8; *M*, 205. Calc. : C, 47·1 ; H, 5·9% ; *M*, 204). The identity of this acid was confirmed by the preparation of the anhydride, m. p. 142°.

(ii) *With potassium permanganate.* To a solution, at 0—5°, of the *cyclo*pentene acid (5 g.) in aqueous sodium carbonate through which a current of carbon dioxide was passing, 2·5% potassium permanganate solution (equiv. to 1 O_2) was added; the colour then remained permanent for 5 minutes. The filtered solution was concentrated in a current of carbon dioxide, acidified, and repeatedly extracted with ether and the extracts were dried and evaporated; a viscid brown oil remained which partly crystallised. This was triturated with concentrated hydrochloric acid, which removed a readily soluble brown oil (Z), and the residue was drained on porous porcelain and recrystallised from hydrochloric acid or from acetone–benzene; a *ketodicarboxylic acid* was thus obtained in glistening prisms, m. p. 182—183°, softening at 177° (Found : C, 56·4, 56·9; H, 6·0, 5·8 ; *M*, 212·6. $C_{10}H_{12}O_5$ requires C, 56·6 ; H, 5·6 ; *M*, 212). This acid was readily soluble in water, alcohol, ethyl acetate, or acetone, and more sparingly soluble in benzene or chloroform. It was slowly attacked by hot chromic acid solution, did not absorb bromine in acetic acid solution, and rapidly decolorised an alkaline solution of potassium permanganate at room temperature. It was readily oxidised by sodium hypobromite with formation of bromoform and carbon tetrabromide; the acid resulting from the oxidation was a gum which contained bromine and was not further examined. The salts of the keto-acid are readily soluble in water.

The *oxime* crystallised in small plates, decomp. 214°, containing apparently $\frac{1}{2}H_2O$ which it did not lose at 100° (Found : C, 50·6, 50·7 ; H, 5·8, 6·2. $C_{10}H_{13}O_5N,\frac{1}{2}H_2O$ requires C, 50·8; H, 5·9%). The *semicarbazone* crystallised from dilute alcohol in microscopic prisms, decomp. 241° (Found : C, 48·8; H, 5·9. $C_{11}H_{15}O_5N_3$ requires C, 49·1 ; H, 5·6%).

The keto-acid, on oxidation with nitric acid (*d* 1·2), gave an excellent yield of γ-methylbutane-αβγ-tricarboxylic acid.

γ-Acetyl-γ-methylbutane-αβ-dicarboxylic Acid (XVII).—The hydrochloric acid solution (Z, above) gave, after the removal of the solvent in a vacuum over potassium hydroxide, a viscid brown oil. This (7 g.) was oxidised in sodium carbonate solution with potassium permanganate at 15—20°. Repeated extraction of the filtered, concentrated, and acidified solution with ether yielded an oil which partly crystallised. The solid was collected and recrystallised from dry ether, in which it was only sparingly soluble, *γ-acetyl-γ-methylbutane-αβ-dicarboxylic acid* separating in fine, glistening prisms, m. p. 125—126°. This acid was readily soluble in water or alcohol, but sparingly soluble in benzene or light petroleum. It did not react with phenylhydrazine or semicarbazide (Found: C, 53·1; H, 7·2. $C_9H_{14}O_5$ requires C, 53·5; H, 6·9%).

When a solution of the sodium salt of the keto-acid was treated with the calculated quantity of a solution of sodium hypobromite, bromoform immediately separated. After 1 hour, this was removed and the alkaline solution was acidified and extracted with ether; the oil obtained on removal of the solvent immediately crystallised and was identified as γ-methylbutane-αβγ-tricarboxylic acid.

*Methyl 5-Oximino-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylate* (XIX).—Methyl *d*-2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylate (0·5 g.) was dissolved in ether containing finely divided sodium (0·06 g.), and to the well-cooled mixture *iso*amyl nitrite (0·26 g.) in ether was added. After the mixture had been kept at 0° for 12 hours the sodium had completely dissolved and a flocculent, yellow precipitate had separated. Ice was then added and the yellow, aqueous solution was separated and acidified. The brown oil obtained (0·3 g.), which showed no tendency to crystallise, was analysed after being kept for some days in a vacuum over sulphuric acid. The first and the second analysis refer to specimens prepared from the crystalline and the liquid ester, respectively (Found: N, 6·5, 6·7. $C_{11}H_{17}O_4N$ requires N, 6·2%). The *oximino-ester* was soluble in all the ordinary organic solvents and in a solution of potassium hydroxide, but was insoluble in aqueous sodium carbonate; it gave with alcoholic ferric chloride a deep brown coloration.

The ester * was hydrolysed by treatment with formaldehyde and hydrochloric acid, followed by dilute aqueous potassium hydroxide; the viscid oil obtained gave with ferric chloride a dirty bluish-green coloration. On keeping, the oil partly crystallised, but, as the quantity of material available was small, no attempt was made at purification and the oil was converted directly into 4 : 4 : 5-

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* During the hydrolysis with potassium hydroxide amyl alcohol separated, indicating that "alcoholysis" with partial formation of the amyl ester had taken place during the reaction with amyl nitrite.

trimethyl-Δ^5-*cyclo*pentene-1 : 3-dicarboxylic acid by the methods already described. The *cyclo*pentene acid prepared in this manner crystallised from methyl alcohol in the characteristic rhombohedra, m. p. 257—258°, and was identical in every way with the acid prepared from the dibromo-ester.

1-4-*Acetyl*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic Acid* (XX) [with ASWATH NARAIN RAO].—A mixture of camphorquinone (25 g.), acetic anhydride (75 c.c.), and freshly-fused zinc chloride (5 g.) was heated on a sand-bath, a vigorous reaction taking place with effervescence and evolution of heat. As soon as the reaction started, the source of heat was removed and the dark brown solution was allowed to cool, diluted with water (150 c.c.), and warmed on the water-bath for a short time to decompose the acetic anhydride. After 12 hours, the pale yellow precipitate of needles and tar was collected and washed with water (yield, 25·5 g.). The filtrate, on neutralisation of the excess of acetic acid with solid sodium carbonate, deposited a further quantity of solid (1 g.). The crude product was repeatedly extracted with dilute sodium carbonate solution until a test portion no longer gave a precipitate on acidification. The residue was extracted with dilute sodium hydroxide solution, which left undissolved camphorquinone (5·4 g.) and a little tar. The sodium hydroxide solution, on acidification, deposited a resinous mass which could not be purified. The deep brown sodium carbonate extract was carefully acidified with dilute sulphuric acid; after the addition of a small quantity of acid, the solution was extracted with ether to remove resinous impurities; on further addition of acid, an oil was deposited which, on evaporation of the dissolved ether, solidified. The crude acid (13·2 g.) was crystallised from hot water, dilute alcohol, or, preferably, light petroleum (b.p. 60—80°), 1-4-*acetyl*-2 : 2 : 3-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic acid* separating in colourless, transparent, glistening laminæ, m. p. 109—111° (Found: C, 63·2; H, 8·3; *M*, 224. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%; *M*, 226). In chloroform solution (1·283 g. in 25 c.c.), it showed $[\alpha]_D$ —66·3°, and this value did not alter during 48 hours. In carbon tetrachloride solution the acid absorbed an equivalent weight of bromine, hydrogen bromide being evolved, and on evaporation of the solvent a sharp-smelling oil remained. In alkaline solution, the acid was unstable to potassium permanganate; the products of the reaction could not be identified.

A solution of the acid (1 g.) in 15% sodium hydroxide solution (8 c.c.) was heated on the water-bath for 3 hours. On acidification of the cooled solution, an oil was precipitated which partly solidified over-night. The solid was separated, drained on porous porcelain, and recrystallised from water; it was then obtained in needles,

m. p. 69—70°. The anhydrous acid melted at 97—98°. It yielded a semicarbazone, m. p. 227—228°, and was identified as 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylic acid by direct comparison with an authentic specimen. The oil extracted from the porous porcelain on which the keto-acid had been drained gave no colour with ferric chloride and evidently contained no hydroxy-acid. The enolic form, therefore, would appear to be incapable of existence. Attempts were made to acetylate the keto-acid directly, but in all cases the acid was recovered unchanged.

The authors wish to thank Dr. M. O. Forster, F.R.S., for much kindly criticism and also for permission to publish the experiments on *l*-4-acetyl-2 : 2 : 3-trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid, which were carried out under his direction.

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[*Received, October* 11*th*, 1926.]

XV.—*Substitution Products of 2-Aminodiphenyl.*

By HAROLD ARCHIBALD SCARBOROUGH and WILLIAM ALEXANDER WATERS.

THE orientation of substituents in 2-acetamido- and in 2-aminodiphenyl forms the second part of a series of investigations on the substitution products of the monoacid bases of the diphenyl series, of which the first part (J., 1926, 557) deals with the products of chlorination and bromination of 4-acetamido- and of 4-aminodiphenyl.

The only substitution product of 2-aminodiphenyl on record is a chlorinated base obtained by Hübner (*Annalen*, 1881, **209**, 339) on reduction of 2-nitrodiphenyl with tin and hydrochloric acid. The salts of this base were analysed, but no attempt was made to assign to it a definite structure. Later investigators, using less drastic methods for the reduction, have been unable to confirm the formation of such a base.

The scope of the present work was, first, a reinvestigation of the methods used in the reduction of 2-nitrodiphenyl, and, secondly, the preparation of the chloro-, bromo-, and nitro-derivatives of 2-acetamido- and of 2-amino-diphenyl.

On reduction of 2-nitrodiphenyl under normal conditions, substitution products of the base were not formed, but on reduction with tin and hydrochloric acid under conditions favourable to indirect chlorination (compare Blanksma, *Rec. trav. chim.*, 1906, **25**,

365) a mixture of approximately 60% of 5-chloro-2-aminodiphenyl and 40% of 2-aminodiphenyl was produced.

Direct chlorination of 2-aminodiphenyl in carbon tetrachloride solution proceeded smoothly and gave a quantitative yield of 3 : 5-dichloro-2-aminodiphenyl hydrochloride. Direct chlorination of the acetylated base invariably yielded gummy products, from which were isolated mixtures of 5-chloro-2-acetamidodiphenyl and unchanged 2-acetamidodiphenyl; and a prolonged action of chlorine yielded a tar from which a pure substance could not be isolated.

2-Acetamidodiphenyl yielded a stable *N*-chloroamine, which could be converted, on treatment with alcohol and acetic acid, into a mixture of 5-chloro-2-acetamidodiphenyl and 2-acetamidodiphenyl. This partly chlorinated mixture could not be separated into its components on account of the very slight differences in solubility of the two substances in all the usual organic solvents. By treating the mixture with sodium hypochlorite, a *N*-chloroamine was formed by both substances, and on conversion with acetic acid in alcohol pure 5-chloro-2-acetamidodiphenyl was obtained. Free chlorine was observed during the conversion, and this fact may be taken as an indication that *N* : 5-dichloro-2-acetamidodiphenyl cannot be transformed into a dichloro-derivative substituted in either ring. This behaviour is the same as that of *N* : 3-dichloro-4-acetamidodiphenyl (*loc. cit.*).

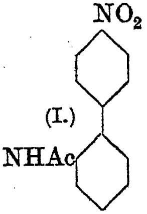
Bromination of the free base in carbon tetrachloride solution yielded 5-bromo-2-aminodiphenyl hydrobromide; bromination in acetic acid solution resulted in a quantitative yield of 3 : 5-dibromo-2-aminodiphenyl, provided that care was taken to remove from the reaction mixture the hydrogen bromide formed. Direct bromination of the base under various conditions did not give a more highly brominated product which could be isolated.

2-Acetamidodiphenyl yielded an impure *N*-bromo-derivative which could not be purified by crystallisation from non-hydroxylic solvents. The impure product on treatment with acetic acid was transformed partly into 5-bromo-2-acetamidodiphenyl and partly into 2-acetamidodiphenyl with the liberation of free bromine.

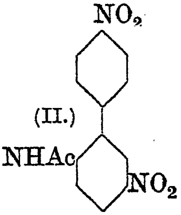
Direct bromination of the acetyl derivative in acetic acid solution at room temperature yielded 5-bromo-2-acetamidodiphenyl; more highly brominated products were obtained in very small yields only on prolonged exposure to sunlight. On bromination at 100°, 3 : 5-dibromo-2-aminodiphenyl was obtained either by the further bromination of the monobromoacetyl derivative and subsequent hydrolysis, or by bromination of 5-bromo-2-aminodiphenyl after hydrolysis had taken place.

On nitration of 2-acetamidodiphenyl in a mixture of acetic acid and sulphuric acid at 0°, an approximately 50% yield of 4′-nitro-2-acetamidodiphenyl (I) was obtained; the residue was a yellow gum from which a crystalline product could not be isolated. By the further nitration of 4′-nitro-2-acetamidodiphenyl, or of the residual gum, a dinitro-2-acetamidodiphenyl was obtained. This product on hydrolysis and deamination yielded 3 : 4′-dinitrodiphenyl (IV), and must therefore have the constitution of a 5 : 4′-dinitro- (II) or of a 3 : 4′-dinitro-2-acetamidodiphenyl (III).

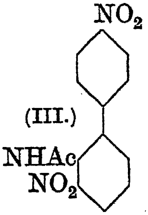
(I.)



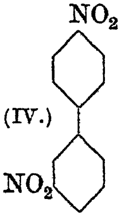
(II.)



(III.)



(IV.)



A conclusive proof of the structure of this dinitro-compound could not be obtained owing to the symmetry of the molecule, but if consideration is given to the chlorination and bromination products of 2-acetamidodiphenyl, it would appear that the most probable structure is 5 : 4′-dinitro-2-acetamidodiphenyl (II).

The structures of the substitution products of 2-aminodiphenyl and of its acetyl derivative are in agreement with those to be expected from an application of the tentative rules for substitution in the diphenyl series which were suggested in the previous communication (*loc. cit.*).

Although it may be seen that the amino-group and groups derived therefrom tend to promote substitution in the same nucleus, yet the nitration of 2-acetamidodiphenyl to yield a product substituted in the 4′-position gives a second instance of substitution in the opposite nucleus when conditions for indirect substitution are not favourable. This anomalous effect can hardly be ascribed to steric influences, since the para-position to the acetamido-group is available, and this position is not adjacent to any large hindering group as was the case in the bromination of 4-acetamidodiphenyl.

EXPERIMENTAL.

2-Aminodiphenyl.—(*a*) 25 G. of 2-nitrodiphenyl (van Hove, *Bull. Acad. Roy. Belg.*, 1922, **8**, 505) were added to a solution of 105 g. of stannous chloride in 500 c.c. of ether obtained by passing in dry hydrogen chloride. After 24 hours, the ether was removed and the base was liberated with sodium hydroxide and distilled in a vacuum (compare Dimroth, *Ber.*, 1907, **40**, 2378).

(*b*) 37 G. of 2-nitrodiphenyl, dissolved in 300 c.c. of alcohol, were added slowly to a solution of 240 g. of stannous chloride in 240 c.c. of concentrated hydrochloric acid. The alcohol was removed after refluxing for 3 hours, and the base liberated and purified as described above.

2-Aminodiphenyl was thus obtained as a white solid, b. p. 170°/15 mm., m. p. 49—50°. Previously recorded values of the m. p. vary between 44° and 49°.

2-*Acetamidodiphenyl* was prepared by adding 1·5 mols. of acetyl chloride drop by drop to a solution of the base in dry pyridine (5 parts) at 0°. After 20 minutes, the mixture was poured into an excess of ice-cold dilute hydrochloric acid. The substance crystallised from dilute alcohol or light petroleum (b. p. 60—80°) in white needles, m. p. 121° (corr.). Previously recorded values of the m. p. vary between 117·5° and 119°. Acetylation of the base by heating with acetic acid or a mixture of acetic acid and acetic anhydride was unsatisfactory, the oily product crystallising only with difficulty and with considerable loss. Samples of 2-aminodiphenyl contaminated with a little 4-aminodiphenyl were acetylated, and the mixed acetyl derivatives treated, in a Soxhlet apparatus, with light petroleum (b. p. 40—60°), in which the 4-acetamidodiphenyl is insoluble.

Chlorination on Reduction of 2-*Nitrodiphenyl.*—A solution of 10 g. of 2-nitrodiphenyl in 100 c.c. of alcohol and 200 c.c. of concentrated hydrochloric acid was boiled under reflux, and granulated tin (10 g.) was added, each piece after the preceding one had dissolved. The alcohol was distilled off and the bases were liberated with sodium hydroxide. The product, isolated and dried in ether, distilled at 170—190°/15 mm. and partly solidified on cooling (Found: Cl, 10·4%, which corresponds with 60% of a monochloro-base). The mixed bases were benzoylated and 5-chloro-2-benzamidodiphenyl, m. p. 142°, was isolated by fractional crystallisation.

3 : 5-*Dichloro*-2-*aminodiphenyl.*—A slight excess of a saturated solution of chlorine in carbon tetrachloride was added to an ice-cold 5% solution of 2-aminodiphenyl in the same solvent. The white precipitate which separated was collected after an hour, washed with carbon tetrachloride, and dried in the air; 3 : 5-*dichloro*-2-*aminodiphenyl hydrochloride* was then obtained, m. p. 140—145° (decomp.) (Found: HCl, 13·4. $C_{12}H_9NCl_2,HCl$ requires HCl, 13·3%). Warming with dilute ammonia gave 3 : 5-*dichloro*-2-*aminodiphenyl*, which crystallised from dilute alcohol in white needles, m. p. 51° (Found: Cl, 29·6. $C_{12}H_9NCl_2$ requires Cl, 29·8%). On benzoylation (Schotten–Baumann) 3 : 5-*dichloro*-2-*benzamidodiphenyl* was obtained, which crystallised from alcohol in long needles, m. p. 207° (Found: Cl, 20·7. $C_{19}H_{13}ONCl_2$ requires Cl, 20·7%).

Chlorination in acetic acid solution yielded tar-like products from which crystalline compounds could not be obtained.

3 : 5-*Dichlorodiphenyl*, obtained from 3 : 5-dichloro-2-aminodiphenyl hydrochloride by the elimination of the amino-group in the usual manner, was a pale yellow oil, b. p. 180°/15 mm. On oxidation with chromic anhydride in glacial acetic acid solution, it yielded 3 : 5-dichlorobenzoic acid, m. p. 188°.

N-*Chloro-2-acetamidodiphenyl.*—To a suspension of 10·6 g. of 2-acetamidodiphenyl in a solution of 20 g. of sodium bicarbonate in 200 c.c. of water, 150 c.c. of *N*-sodium hypochlorite were added during 2 hours. The precipitate was collected after 12 hours, washed with cold water, dried, and fractionally crystallised from light petroleum (b. p. 40—60°), the more soluble fraction being preserved. The *chloroamine* was thus obtained in colourless needles, m. p. 86° (Found: available Cl, 13·9. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

Conversion of the N-*Chloroamine.*—A mixture of 5 g. of the chloroamine, 100 c.c. of alcohol, and 5 c.c. of glacial acetic acid was warmed gently until it gave no reaction with potassium iodide. Water was then added to start precipitation, and the solid matter which separated on cooling was crystallised fractionally from light petroleum (b. p. 60—80°), and also from dilute aqueous solutions of alcohol, acetone, and acetic acid. The product formed white crystals which melted over the range 110—120° according to the specimen, but it was not possible to separate the constituents: m. p. after two crystallisations, 116° (Found: Cl, 11·6%); m. p. after six crystallisations, 120° (Found: Cl, 12·2%); m. p. of another preparation, 118° (Found: Cl, 10·4%). $C_{14}H_{12}ONCl$ requires Cl, 14·4%.

By treatment of the mixture with sodium hypochlorite, followed by conversion with dilute acetic acid as previously described, chlorine was evolved and pure *5-chloro-2-acetamidodiphenyl* was obtained, which crystallised from dilute alcohol or light petroleum in long needles, m. p. 122·5° (Found: Cl, 14·6. $C_{14}H_{12}ONCl$ requires Cl, 14·4%). From this substance, *5-chloro-2-benzamidodiphenyl* was obtained, which crystallised from dilute alcohol in colourless needles, m. p. 142—143° (Found: Cl, 11·6. $C_{19}H_{14}ONCl$ requires Cl, 11·5%).

The yield of crystalline solids in both *N*-chloroamine transformations was small, as the residues from the crystallisation were dark oils from which pure substances could not be separated.

Direct Chlorination of 2-Acetamidodiphenyl.—A 2% solution of 2-acetamidodiphenyl in glacial acetic acid, containing a large excess of anhydrous sodium acetate, was cooled in water and a mixture of chlorine and carbon dioxide was passed in slowly until the gain in weight corresponded to the formation of a monochlorinated compound; the mixture was then poured on to ice and water. A yellow gum separated which became semi-solid and crystallised from light petroleum as a white powder consisting of 5-chloro-2-acetamidodiphenyl and 2-acetamidodiphenyl. A similar mixture was obtained by chlorination in carbon tetrachloride solution. A solid could not be separated if the chlorination was carried on to a higher stage of substitution.

2 : 5-*Dichlorodiphenyl*.—5 G. of 5-chloro-2-acetamidodiphenyl were hydrolysed by boiling for a day with 10% alcoholic hydrochloric acid. The hydrochloride of the base, which separated after the removal of the alcohol, was converted into the corresponding dichlorodiphenyl by the Sandmeyer reaction. A light yellow oil (2 g.) was obtained, b. p. 171°/15 mm. (Found : Cl, 31·25. $C_{12}H_8Cl_2$ requires Cl, 31·8%). This crude product was oxidised by chromic anhydride in glacial acetic acid solution to 2 : 5-dichlorobenzoic acid, m. p. 154°.

N-*Bromo-2-acetamidodiphenyl* was prepared in a similar manner to the corresponding chloro-compound. It was a pale yellow powder, easily soluble in non-hydroxylic solvents, and could not be obtained of a greater purity than about 70%. On treatment with alcohol and acetic acid, it decomposed with the liberation of bromine, and yielded a mixture of 5-bromo-2-acetamidodiphenyl, m. p. 130°, and 2-acetamidodiphenyl.

5-*Bromo-2-acetamidodiphenyl*.—A cold 10% solution of 2-acetamidodiphenyl in glacial acetic acid was treated with bromine (1 mol.) as a 10% solution in the same solvent. After 1 day, the mixture was poured into water; the brominated compound, which was precipitated in an almost quantitative yield, crystallised from dilute alcohol in white needles, m. p. 130° (Found : Br, 27·7. $C_{14}H_{12}ONBr$ requires Br, 27·6%).

By the hydrolysis of this acetyl derivative with 10% alcoholic hydrobromic acid *5-bromo-2-aminodiphenyl* was obtained. It crystallised from dilute alcohol in white needles, m. p. 57·5° (Found : Br, 32·0; C, 58·1; H, 4·15. $C_{12}H_{10}NBr$ requires Br, 32·1; C, 58·1; H, 4·0%). This base on benzoylation (Schotten–Baumann) gave *5-bromo-2-benzamidodiphenyl*, which crystallised from alcohol in white needles, m. p. 162° (Found : Br, 22·9. $C_{19}H_{14}ONBr$ requires Br, 22·7%).

2 : 5-*Dibromodiphenyl*, obtained from 5-bromo-2-aminodiphenyl by the Sandmeyer reaction, was a yellow oil, b. p. 209°/15 mm., which became very viscous but did not solidify on cooling to 0° (Found : Br, 51·4. $C_{12}H_8Br_2$ requires Br, 51·3%). On oxidation

with chromic anhydride in glacial acetic acid solution it yielded 2 : 5-dibromobenzoic acid, m. p. 156°.

5-Bromo-2-aminodiphenyl Hydrobromide.—A 10% solution of 2-aminodiphenyl in carbon tetrachloride was treated with slightly more than one molecular equivalent of bromine as a 5% solution in the same solvent. The light yellow precipitate which formed was filtered off after an hour, washed with carbon tetrachloride, and dried in the air. It had a m. p. of 226°, but it could not be crystallised on account of the ease with which it was hydrolysed (Found : HBr, 24·4. $C_{12}H_{10}NBr,HBr$ requires HBr, 24·6%). On treatment with ammonia, it yielded the corresponding base as a viscous oil. This, on benzoylation, gave 5-bromo-2-benzamidodiphenyl, which alone or mixed with a specimen prepared by the alternative method melted at 161—162°.

3 : *5-Dibromo-2-aminodiphenyl.*—To 5 g. of 2-aminodiphenyl, dissolved in 50 c.c. of glacial acetic acid, 5 g. of powdered anhydrous sodium acetate were added and the mixture was cooled in ice-water while 100 c.c. of a 10% solution of bromine in glacial acetic acid were run in slowly until the bromine was no longer decolorised. The mixture was poured on to ice and water. The brown oil thrown down soon solidified and crystallised from dilute alcohol in needles, m. p. 51—52° (Found : Br, 48·8. $C_{12}H_9NBr_2$ requires Br, 48·9%). The yield is quantitative, but if no sodium acetate be added to remove the hydrogen bromide produced by the reaction only viscous black oils can be obtained.

The *benzoyl* derivative crystallised from alcohol in white needles, m. p. 218° (Found : Br, 37·0. $C_{19}H_{13}ONBr_2$ requires Br, 37·1%). On eliminating the amino-group from the base in the usual manner 3 : *5-dibromodiphenyl*, b. p. 208°/15 mm., was obtained (compare J., 1926, 561). It was oxidised to 3 : 5-dibromobenzoic acid, m. p. 212°.

Further Bromination of 5-Bromo-2-acetamidodiphenyl.—Only small traces of more highly brominated products could be obtained by exposing a solution of 5-bromo-2-acetamidodiphenyl and bromine, containing a little iodine as a catalyst, to sunlight for more than a week. On heating the mixture to 100°, bromination occurred together with hydrolysis of the acetyl derivative, for, on pouring the product into water, a dark oil separated which, on benzoylation, yielded 3 : 5-dibromo-2-benzamidodiphenyl; this melted at 218°, alone or mixed with a sample prepared by the alternative method.

Nitration of 2-Acetamidodiphenyl.—15 G. of 2-acetamidodiphenyl, dissolved in 15 c. c. of glacial acetic acid and 30 c.c. of concentrated sulphuric acid at 0°, were slowly treated with a mixture of 6 c.c. of fuming nitric acid and 14 c.c. of glacial acetic acid. After an hour, the product was poured on to ice; the yellow solid was filtered off, washed with dilute sodium carbonate solution, and fractionally crystallised from alcohol; 8 g. of pale yellow needles, m. p. 199°, were thus obtained, consisting of *4′-nitro-2-acetamidodiphenyl* (Found: N, 10·8. $C_{14}H_{12}O_3N_2$ requires N, 10·9%). The residual alcoholic solutions, on evaporation, yielded a reddish-yellow gum from which it was not possible to isolate any other substitution product.

By the hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid, *4′-nitro-2-aminodiphenyl* was obtained. It crystallised from alcohol in orange-red needles, m. p. 158° (Found: N, 13·3. $C_{12}H_{10}O_2N_2$ requires N, 13·1%).

4′-Nitro-2-bromodiphenyl, obtained from the base by the Sandmeyer reaction, crystallised from alcohol in bright yellow needles, m. p. 82·5° (Found: Br, 28·5. $C_{12}H_8O_2NBr$ requires Br, 28·7%). On oxidation with chromic anhydride in glacial acetic acid solution, bromine was evolved and *p*-nitrobenzoic acid was produced, m. p. 240—241°.

Dinitration of 2-Acetamidodiphenyl.—The nitration was carried out under conditions similar to those given above, but with the use of a double quantity of nitric acid, and the mixture was kept for 24 hours before the products were separated. The solid product was extracted with alcohol, and the insoluble residue was crystallised from benzene; it then formed pale yellow prisms, m. p. 211°, of 5(or 3) : *4′-dinitro-2-acetamidodiphenyl* (Found: N, 14·1. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). This substance yielded *p*-nitrobenzoic acid (m. p. 240—241°) on oxidation with chromic and glacial acetic acids, showing that one of the nitro-groups was in the 4′-position.

The same dinitro-compound could be isolated by further nitration of the gum produced in the less drastic nitration reaction, but in no case was the total yield more than 60%. The residue consisted of the usual, more soluble, oily products. On hydrolysis with alcoholic hydrochloric acid, the *base* corresponding to the acetyl derivative was obtained. It separated from alcohol as a bright yellow powder, m. p. 238° (Found: N, 16·35. $C_{12}H_9O_4N_3$ requires N, 16·2%).

By eliminating the amino-group from this compound by the usual method, *3 : 4′-dinitrodiphenyl* was obtained; it melted at 189°, alone or mixed with a specimen obtained by the elimination of the amino-group from 3 : 4′-dinitro-4-aminodiphenyl.

All the m. p.'s recorded in this paper have been corrected, and where necessary the identity of a substituted benzoic acid has been established by the "mixed m. p." method.

The authors beg to thank the Chemical Society for a grant from the Research Fund. One of the authors (W. A. W.) desires to thank the Master and Fellows of Gonville and Caius College for a studentship, and the Advisory Council of the Department of Scientific and Industrial Research for a grant, which have enabled him to collaborate in this work.

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CAMBRIDGE. [*Received, November* 13*th*, 1926.]

XVI.—*The Vapour Pressures of Mixtures of* (a) *Methyl Acetate and Water;* (b) *Methyl Acetate, Sucrose, and Water.*

By ANDREW MCKEOWN and FLAXNEY PERCIVAL STOWELL.

THE measurements now recorded were carried out with the primary object of testing various "activity" theories of reaction velocity in the special case of the hydrolysis of methyl acetate by acids. Whilst no satisfactory conclusions could be drawn from their application in this connexion, the data may be of value from the point of view of thermodynamic theory, or they may be of use to other workers in the field of chemical kinetics.

The activities of the two volatile constituents in ester–water and ester–sucrose–water mixtures have been obtained by measurement of their partial vapour pressures, which represent the respective activities with sufficient accuracy for most purposes. As a check, the total vapour pressure of each system investigated has also been determined by an independent method. In the case of ester–water mixtures, concentrations of ester up to about $2N$ have been used. All the ester–sucrose–water mixtures contained a constant small concentration of ester, the sucrose content varying up to 600 g. per litre of solution. This involves a considerable variation in the concentration of water. All measurements have been carried out at two temperatures, *viz.*, 25° and 35°.

EXPERIMENTAL.

Total Vapour Pressures.—The static method of measurement adopted was very similar to that proposed by Morton (*J. Soc. Chem. Ind.*, 1919, **38**, 363T). A few practical modifications may be mentioned. In place of the jacketing arrangement indicated in Morton's diagram, the two barometer tubes and the capillary tubes attached to their upper ends pass through the bottom of a thermostat maintained at the working temperature. The lower ends of the barometer tubes dip below the surface of mercury in a closed container. This arrangement avoids the necessity for rubber joints and connexions and consequent fouling of the mercury. A small sealed glass stirrer containing a bundle of soft-iron rods is placed in the barometer tube which contains the experimental mixture. This stirrer, operated from outside by an electromagnet, facilitates the removal from the liquid of dissolved air, which is then pumped out through the capillary. Before the hydrostatic levels of mercury and solution in the tubes are read, the stirrer is lifted out of the solution and suspended above its surface by means of the electromagnet. The levels are read off through a telescope on an accurately graduated glass scale placed behind the tubes. In order to dispense with the precautions necessary to ensure a complete vacuum in the comparison tube (a trace of moisture in this would, of course, lead to erroneous results), it has been found convenient to retain a few c.c. of air-free water over the mercury surface in this tube. The vapour pressure of the mixture under examination is then compared, not against zero pressure, but against the pressure of saturated aqueous vapour at the same temperature. A glass tap at the end of the capillary tube attached to the comparison tube prevents the expulsion of this water at each pumping operation which is carried out for the other tube.

For the purpose of vapour-pressure measurements, the purest methyl acetate is essential. Kahlbaum's ester was therefore purified by the method recommended by Young and Thomas (J., 1893, **63**, 1191). The pure product distilled between 56·9° and 57·1° (standardised thermometer) at 760 mm. (Young and Thomas give 57·1°.) The vapour pressure of the pure ester was 214·9 mm. at 25° and 328·6 mm. at 35°, as compared with 215·0 and 327·5 mm., respectively, interpolated from Young and Thomas's data. The ester had $d_{4^\circ}^{15^\circ}$ 0·9355 (compare 0·9359, given by the same authors).

Table I gives the total vapour pressures of various ester–water mixtures at 25° and 35°. The normalities refer to 15°, and the pressures are expressed in mm. Hg at 0°. Each figure represents the mean of a number of determinations with different samples of duplicate stock solutions. The variation from this mean was usually of the order ±0·2%, and this probably represents the maximum error in the data. Table II contains the total vapour pressures of ester–sucrose–water mixtures, each of which was 0·2542*N* with respect to ester. With increasing sucrose content, duplication became less satisfactory, probably owing to increasing difficulty in getting rid of dissolved air as the solutions became more viscous, and the possible error in the data for the highest concentrations of sucrose is about ±0·5%.

From Table II it is seen that the total vapour pressure of a solution which is 0·2542*N* with respect to ester rises rapidly as the sucrose

TABLE I.

Total Vapour Pressures of Ester–Water Mixtures at 25° and 35°.

Mols. of ester per litre of soln.	Mols. of water per litre of soln.	Total vapour pressure	
		at 25°.	at 35°.
0	55·4	23·8	42·2
0·2542	54·5	46·0	80·2
0·5084	53·6	67·2	115·9
1·017	51·6	108·2	176·8
1·525	49·4	144·2	225·1
2·033	47·3	172·2	265·4
Pure ester.	—	214·9	328·6

TABLE II.

Total Vapour Pressures of Ester–Sucrose–Water Mixtures at 25° and 35°.

(Constant concentration of ester = 0·2542 mol./litre.)

G. of sucrose per litre of soln.	Mols. of water per litre of soln.	Total vapour pressure	
		at 25°.	at 35°.
0	54·5	46·0	80·2
100	51·0	48·2	83·2
200	47·6	51·4	87·3
300	44·1	55·6	92·8
400	40·7	60·5	99·5
500	37·2	66·7	108·0
600	33·6	75·5	120·8

content increases. This effect is not unexpected in view of the marked displacing effect of the sucrose in solution. This produces a very appreciable increase in the molar fraction of the more volatile component—the ester—with increasing concentration of sucrose.

Partial Vapour Pressures.—These have been determined by the well-known dynamical method. This involves the saturation of a known volume of an indifferent gas with the vapours in equilibrium with the liquid mixture under examination and analysis of the resulting gaseous mixture. In the present work, estimation by a direct absorption method of the amount of each component carried over as vapour is rendered impossible by the fact that the ester vapour would react with any of the reagents normally used for the removal of water vapour. An indirect method of analysis, depending on the combustion of the mixed vapours and subsequent estimation of the products of combustion, was therefore adopted. The same method has been employed by Linebarger (*J. Amer. Chem. Soc.*, 1895, **17**, 615), by Foote and Scholes (*ibid.*, 1911, **33**, 1309), and by Wright (J., 1922, **121**, 2251). The data obtained by Foote and Scholes for the partial vapour pressures of ethyl alcohol and water over alcohol–water mixtures indicate that, with suitable precautions, a fair degree of accuracy can be obtained by this mode of analysis.

Details of the experimental method need not be given. The main features of the technique involve an accurate knowledge of the volume, temperature, and pressure of the air which is to be saturated, and of the pressure of the gas mixture when it leaves the last saturator; the use of an efficient train of saturators; the introduction of an auxiliary oxygen supply beyond the last of these; prevention of condensation of the vapours from the saturated air current; and the usual precautions incidental to combustions.

The partial vapour pressures p_e and p_w of ester and water respectively are given by the relations:

$$p_e = xR\theta(P + p_m - p_s)/132PV,$$
$$p_w = (y - 0{\cdot}4095x)R\theta(P + p_m - p_s)/18PV,$$

where x and y are the weights of carbon dioxide and water resulting from saturation of V litres of dry air measured under atmospheric pressure, P, and at the working temperature θ° Abs., p_m is the working pressure in excess of atmospheric as registered on an auxiliary manometer beyond the last saturator, p_s is the total vapour pressure of the solution, and R is the gas constant expressed in litre-millimetres. In the above equations, the value of p_s already obtained by the static method may be employed, or, alternatively, we need not assume that p_s is known, but substitute $p_s = p_e + p_w$, and solve the two simultaneous equations for p_e and p_w. These methods of calculation lead to substantially the same values of p_e and p_w.

Any experimental error usually affects the value obtained for the partial pressure of water much more than that of ester. The value of p_w is determined by difference between the total water found and the water corresponding to combustion of the ester vapour, and the latter quantity is usually several times greater than the weight of water corresponding to p_w. Hence any error in the estimation of the carbon dioxide (which determines the value of p_e) produces a much greater error in the value of p_w. In the case of the highest concentrations of ester used, an error of 1 mg. in the weight of the carbon dioxide would only affect the value of p_e by 0·1%, but would introduce a 4% error into p_w. The partial pressure of the water might, of course, be obtained indirectly by subtraction of the observed partial pressure of ester from the total vapour pressure of the solution independently obtained.

Tables III and IV contain the results for ester–water and ester–sucrose–water mixtures, respectively, at 25° and 35°. In cols. 2 and 3 of the tables the sum of the observed partial pressures p_e and

p_w is compared with the total vapour pressure p_s obtained by the static method.

TABLE III.

Partial Vapour Pressures of Ester and Water over Ester–Water Mixtures.

Conc. of ester.	p_s.	$p_e + p_w$ (obs.).	p_e. (obs.).	p_e (calc.).	p_w (obs.).	p_w (calc.).
At 25°.						
0·2542	46·0	46·5	22·5	22·3	24·0	23·7
0·5084	67·2	67·8	43·7	43·7	24·1	23·5
1·017	108·2	108·8	85·3	84·9	23·5	23 3
1·525	144·2	144·8	122·0	121·1	22·8	23·1
2·033	172·2	172·5	149·2	149·4	23·3	22·8
At 35°.						
0·2542	80·2	80·4	38·3	38·2	42·1	42·0
0·5084	115·9	115·8	73·9	74·1	41·9	41·8
1·017	176·8	176·4	134·8	135·4	41·6	41·4
1·525	225·1	224·5	183·9	184·2	40·6	40·9
2·033	265·4	267·5	226·6	224·9	40·9	40·5

TABLE IV.

Partial Vapour Pressures of Ester and Water over Ester–Sucrose–Water Mixtures.

(Constant concentration of ester = 0·2542N.)

G. of sucrose per litre of soln.	p_s.	$p_e + p_w$. (obs.).	p_e. (obs.).	p_e. (calc.).	p_w. (obs.).	p_w. (calc.).
At 25°.						
0	46·0	46·5	22·5	22·3	24·0	23·7
100	48·2	48·1	24·6	24·7	23·5	23·5
200	51·4	51·4	28·1	28·1	23·3	23·3
300	55·6	55·5	32·3	32·5	23·2	23·1
At 35°.						
0	80·2	80·4	38·3	38·2	42·1	42·0
100	83·2	82·8	41·3	41·5	41·5	41·7
200	87·3	87·4	45·6	45·9	41·8	41·4
300	92·8	92·2	51·5	51·7	40·7	41·1
400	99·5	99·4	58·6	58·9	40·8	40·6

Discussion of Results.

The values given under p_e (calc.) and p_w (calc.) in Table III are derived as follows. The highest concentration of ester employed is 2·033N, and represents a molar fraction of ester of 0·04117. All the mixtures used are therefore relatively dilute solutions of ester in water and should conform more or less to Raoult's law, *i.e.*, the partial pressure of the solvent water should be approximately equal to the vapour pressure of pure water multiplied by the molar fraction of water in the solution. This gives p_w (calc.), and, subtracting this from the total vapour pressure p_s, the value of p_e (calc.) is obtained.

The general agreement between the observed and the calculated partial pressures in Table III indicates that Raoult's law is valid as a rough approximation for the solvent. It cannot, however, be strictly applicable over the whole range studied, since Henry's law is not obeyed by the solute. The curve obtained by plotting p_e against the molar fraction of ester (N_e) is uniformly concave to the N_e-axis. If we make the probable assumption that very dilute solutions of ester in water obey Raoult's law, it can readily be shown that over the same range of concentration the plot of p_w against N_e is convex to the N_e-axis. This implies that p_w (obs.) should always be greater than p_w (calc.), and that the divergence should be greater the greater the concentration of ester. Our experimental data for p_w (obs.), however, are not sufficiently accurate to afford a test of this point.

Considerable difficulty was experienced in obtaining trustworthy results for ester–sucrose–water mixtures. For solutions of high sucrose content the results were altogether untrustworthy, the partial pressure of ester being abnormally small and that of the water abnormally great. This is just what would be expected if the air current were incompletely saturated with the mixed vapours, and it is probable that the train of saturators used was not efficient enough for the more viscous sucrose solutions. Such data as appear to be trustworthy are in Table IV. As in the case of the ester–water mixtures, the experimental values of the partial pressures are compared with the figures calculated on the assumption that the component water obeys Raoult's law. In estimating the molar fraction of water present, it has been assumed that the sucrose molecule is hydrated by four molecules of water. A fair agreement exists between the observed and the calculated partial pressures. Such agreement is to be expected since (*a*) the concentration of ester is in all cases small, so that, in so far as it affects the partial pressure of the water, Raoult's law should apply as a close approximation; (*b*) the observed vapour pressures of aqueous solutions of sucrose over a considerable range of sucrose content may be calculated fairly accurately from Raoult's law, assuming the above hydration.

Returning to the ester–water case, an interesting point arises when the observed values of p_e at various concentrations of ester are compared at the two temperatures 25° and 35°. The ratio $p_e(35°)/p_e(25°)$ decreases as the concentration or molar fraction of ester increases (see Table V). This means that the latent heat of vaporisation of ester from its aqueous solutions decreases with increasing molar fraction of ester. The same result is obtained if, with a constant concentration of ester, its molar fraction is artificially increased by addition of sucrose. Table VI shows this decrease in the ratio $p_e(35°)/p_e(25°)$ with increasing sucrose content.

TABLE V.

Conc. of ester (mols. per litre).	$p_e(35°)/p_e(25°)$.
0·2542	1·70
0·5084	1·69
1·017	1·58
1·525	1·53
2·033	1·52
Pure ester.	1·53

TABLE VI.

(Constant conc. of ester = 0·2542N.)

Conc. of sucrose (g./litre).	$p_e(35°)/p_e(25°)$.
0	1·70
100	1·68
200	1·62
300	1·59

By applying the Duhem–Margules relation to the data of Table V, it readily follows that the ratio $p_w(35°)/p_w(25°)$ *increases* with increasing ester content, which in turn requires that the relative depression of the vapour pressure of the solvent water by addition of ester should be less the higher the temperature. This result is possibly of significance in relation to the evidence recently offered by Kendall and King (J., 1925, **127**, 1778) for the existence of an ester–water complex in aqueous solutions of ethyl acetate. If a similar complex were present in methyl acetate–water mixtures, increase of temperature would certainly favour its dissociation, and the relative depression of vapour pressure of the water would therefore decrease with increasing temperature. In this connexion might also be mentioned the appreciable contraction in volume accompanying the solution of methyl acetate in water.

Summary.

The partial vapour pressures of methyl acetate and water in ester–water and ester–sucrose–water mixtures have been determined at 25° and 35°.

The total vapour pressures of the same systems have been measured by an independent method at these temperatures.

The nature of the partial-pressure curves suggests appreciable compound formation between water and methyl acetate in aqueous solutions of the ester.

One of us (F. P. S.) desires to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant during the course of this work.

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[*Received, October 16th,* 1926.]

XVII.—*Organic Derivatives of Silicon. Part XXXII. The Carbon–Silicon Binding.*

By Frederic Stanley Kipping.

Fresh evidence is continually being obtained by the author that an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional conditions. Those reactions which lead to the formation of an olefine seem to be quite inapplicable to the production of the group $>Si{:}C<$.

The loss of one molecule of water from one molecule of a tertiary silicol, $R_2Si(OH){\cdot}CH_2R$, is an unknown change; under conditions which have not yet been fully investigated, such silicon compounds, instead of giving $R_2Si{:}CHR$, pass into the corresponding oxides, $(R_2Si{\cdot}CH_2R)_2O$, as, for example, in the cases of benzylethylpropylsilicol, $SiEtPr(CH_2Ph){\cdot}OH$, and phenyldiethylsilicol, $SiEt_2Ph{\cdot}OH$. Many tertiary alcohols, on the other hand, are readily converted into olefines without any production of the corresponding ether.

Again, the loss of halogen acid from the molecule of a chloride, $R_2SiCl{\cdot}CH_2R$, has never been observed; such compounds can be distilled at relatively high temperatures without appreciable decomposition, as, for example, phenylethylpropylsilicyl chloride and tribenzylsilicyl chloride. This behaviour may be contrasted with that of many analogous carbon compounds which lose a molecule of halogen acid very readily, giving olefines; $CMeEt(CH_2Ph)Br$, for example, cannot be distilled even under low pressure. Similarly, many dichloro-derivatives, R_2SiCl_2, such as dibenzylsilicon dichloride distil at relatively high temperatures without decomposing.

The formation of an unsaturated compound by the action of a Grignard reagent on a tertiary silicyl chloride is also unknown; it has been proved in very many cases that a normal reaction occurs with the formation of a quaternary silicane, and, although by-products are nearly always obtained, these are substances of high boiling point; it is, of course, possible that these by-products are formed by the polymerisation of compounds containing the $Si{:}C$ binding, but no evidence of this has been recorded. Many tertiary halogen derivatives, on the other hand, give rise to olefines (Trotman, J., 1925, **127**, 88) so readily that the formation of a saturated quaternary hydrocarbon either does not take place, or it does so only to a very limited extent.

Experiments with the direct object of producing the group $>Si{:}C<$ seem to have been recorded in one instance only. Schlenk and Renning (*Annalen*, 1912, **394**, 221) treated silicon tetrachloride with magnesium phenyl bromide (2 mols.) in order to form diphenyldichlorosilicane, and then heated the crude product with magnesium methyl iodide (1 mol.) in order to obtain diphenylmethylchlorosilicane; afterwards they decomposed this chloride with water and obtained by distillation a liquid boiling at 266—268°/72 mm. From the results of one combustion and a molecular-weight determination they assigned to this liquid the constitution $SiPh_2{:}CH_2$, although it did not react with bromine or with alkaline permanganate.

Now the known behaviour of certain pure silicols of an analogous structure (see above) casts grave doubt on this supposed conversion of diphenylmethylsilicol into an unsaturated compound.

Further, it is the author's experience that when silicon tetrachloride is treated with magnesium phenyl bromide (2—2½ mols.) the product is always a mixture, no matter how slowly the Grignard reagent is added, or whatever other precautions are taken to ensure the formation of the desired substance only. Consequently, since Schlenk and Renning did not purify either the dichloride, $SiPh_2Cl_2$, or the monochloride, $SiPh_2MeCl$, the final crude product must have been a complex mixture of silicon compounds (with diphenyl), from which it would be no easy task to isolate any component.

Schlenk and Renning's experiments have therefore been repeated, but all endeavours have failed to afford the slightest confirmation of their results.

Further attempts to prepare a compound containing the $>Si{:}C<$ group were then made; tribenzylsilicyl chloride was heated with quinoline or with dimethylaniline with the object of eliminating hydrogen chloride; apparently, however, no such change took place. Tribenzylsilicol, as was previously shown (J., 1909, **95**, 308), is unchanged when it is heated with acetic anhydride; further attempts to convert it into an unsaturated compound by heating it with phosphoric oxide or with zinc chloride have likewise given negative results.

EXPERIMENTAL.

To a solution of purified diphenyldichlorosilicane in ether (5 vols.) an ethereal solution of magnesium methyl iodide (1 mol.) was gradually added. There was very little heat developed, and no deposition of magnesium salt occurred, but after some time the liquid had separated into two liquid layers. The next day the ether was distilled, and the residue heated at about 120° during 2 hours; the magnesium salt had then become crystalline. The silicon compound was extracted from the magnesium salt in the usual way in the absence of moisture and was distilled (25 mm.) without fractionating in order to get rid of magnesium salt; a small proportion of a liquid of high boiling point remained in the residue. The whole distillate was then fractionated (45 mm.); it began to boil at 170°, and from 170° to 185° a large fraction was collected. From 185° to 195° very little came over, but above this temperature a considerable proportion of diphenyldichlorosilicane was collected. The fractions 170—185° and 185—200° were separately redistilled many times, but no liquid of constant boiling point could be obtained. Analyses indicated that the portion boiling at 175—180° consisted chiefly of diphenyldimethylsilicane with some diphenylmethylsilicyl chloride; the latter compound was contained principally in the fraction 180—195°, a colourless, mobile liquid which fumed slightly in moist air.

In order to obtain a silicol the very impure chloride was diluted with light petroleum and shaken with either water or potassium hydroxide solution. The product distilled mainly from about 170—190° (45 mm.), and a little passed over up to about 210°, leaving a very small proportion of liquid of high boiling point, which was probably the oxide, but which could not be obtained in crystals; all attempts to isolate from the main fraction either the pure silicol or the unsaturated compound described by Schlenk and Renning were unsuccessful, and every time the liquid was distilled a very small proportion of the residue of high boiling point was formed. The combined fractions were then repeatedly distilled very slowly under atmospheric pressure; during each operation water was formed and a substance (the oxide) of high boiling point; after five such treatments, the distillate having been dried after each, the whole was put back on to the residue and the liquid was heated just below its boiling point during about 2 hours. Water was again formed and removed. Finally, the liquid was distilled (45 mm.); about 80% of the original preparation passed over from 165—185° and the thermometer then rose very rapidly to about 270°, above which temperature a thick, yellow oil was collected. The lower fraction did not decolorise a dilute chloroform solution of bromine, or an aqueous solution of permanganate; these facts, also observed by Schlenk and Renning with their preparation, afford strong evidence of the absence of unsaturated compounds. The higher fraction slowly deposited crystals of *diphenylmethylsilicyl oxide*, $(SiMePh_2)_2O$, which, freed from oil on porous earthenware, separated from cold alcohol in plates having the outline of a regular hexagon, or of a rhomb, and melting at 51—52° (Found: Si, 13·7. $C_{26}H_{26}OSi_2$ requires Si, 13·7%). This oxide is very readily soluble in ether, light petroleum (b. p. 50—60°), acetone, and other common solvents, from which it usually separates as an oil; it is only sparingly soluble in cold alcohol.

These results show that diphenylmethylsilicol is only very slowly decomposed when it is heated at its boiling point, and that, like other silicols of a similar type, it then gives the oxide. Schlenk and Renning's product, obtained apparently after one distillation only, was doubtless a mixture of diphenyldimethylsilicane, diphenylmethylsilicol, and probably diphenyl, and the results of their single analysis can scarcely establish the existence of a compound containing the $>Si{:}C<$ binding.

A pure specimen of *diphenyldimethylsilicane*, $SiMe_2Ph_2$, was prepared by treating diphenyldichlorosilicane with an excess of magnesium methyl iodide in ethereal solution, and then heating the residue at 150°; after cooling and addition of water, the silicon compound separated as an oil, and, on distillation, was obtained as a colourless, fairly mobile liquid with a faint aromatic odour, b. p. 176—178°/45 mm., and miscible with all organic solvents. It was not easy to estimate the silicon in this compound in the usual way, even using bromine or nitric acid in addition to sulphuric acid, all the results being low; good results, however, were obtained on combustion (Found: C, 79·0; H, 7·6. $C_{14}H_{16}Si$ requires C, 79·2; H, 7·5%).

The author is indebted to the Government Grant Committee of the Royal Society for a grant which covered a part of the cost of the materials, and also to Mr. J. E. Sands for assistance in some of the experimental part of this work.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November 20th,* 1926.]

XVIII.—*Reactions of Carbohydrazide. Part I.*

By ANDREW CHARLES BROWN, ERIC CHARLES PICKERING, and FORSYTH JAMES WILSON.

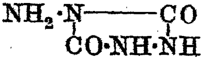
As comparatively little work has been done on the aldehydic and ketonic derivatives of carbohydrazide, we decided, in conjunction with investigations on similar lines, to make a study of these compounds, particularly as regards their thermal decomposition.

The only such derivatives described so far are the dibenzylidene derivative, $CO(NH{\cdot}N{:}CHPh)_2$ (Curtius and Heidenreich, *J. pr. Chem.*, 1895, **52**, 471), and the dibenzophenone derivative, $CO(NH{\cdot}N{:}CPh_2)_2$, a compound tentatively described as such by Borsche and Merkwitz (*Ber.*, 1904, **37**, 3177; compare Wilson and Crawford, J., 1925, **127**, 103), but not synthesised. We have prepared the following carbohydrazones from carbohydrazide and the appropriate ketone: *diacetonecarbohydrazone*, $CO(NH{\cdot}N{:}CMe_2)_2$, *di(methyl ethyl ketone)carbohydrazone*, $CO(NH{\cdot}N{:}CMeEt)_2$, *diacetophenonecarbohydrazone*, $CO(NH{\cdot}N{:}CMePh)_2$, and dibenzophenonecarbohydrazone. By means of carbohydrazide, $CO(NH\cdot NH_2)_2$, we have prepared *carbohydrazones* of the type $CRR'{:}N\cdot NH\cdot CO\cdot NH\cdot NH_2$ (which we designate *δ-aminosemicarbazones*) from benzaldehyde, acetophenone, benzophenone, benzil, and diacetyl; a compound of a mixed type, *benzaldehyde acetophenone carbohydrazone*, $CHPh{:}N\cdot NH\cdot CO\cdot NH\cdot N{:}CMePh$, has also been prepared. Acetylacetone and carbohydrazide gave 3 : 5-dimethylpyrazole.

The thermal decomposition of dibenzaldehydecarbohydrazone, diacetophenonecarbohydrazone, and benzaldehyde-δ-aminosemicarbazone occurred in two stages. In boiling absolute alcoholic solution, dibenzaldehydecarbohydrazone gradually underwent decomposition, giving dibenzaldehydehydrazidicarbohydrazone, already described by Stollé (*Ber.*, 1910, **43**, 2468), and benzylideneazine: $2CO(NH\cdot N{:}CHPh)_2 =$

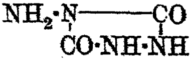
$$CO(NH\cdot N{:}CHPh)\cdot NH\cdot NH\cdot CO(NH\cdot N{:}CHPh) + (CHPh)_2N_2.$$

When heated at its melting point, the carbohydrazone gave 4-aminourazole and benzylideneazine, the intermediate dibenzaldehydehydrazidicarbohydrazone evidently decomposing in this way: $CO(NH\cdot N{:}CHPh)\cdot NH\cdot NH\cdot CO(NH\cdot N{:}CHPh) =$



$\begin{array}{l} NH_2\cdot N\text{———}CO \\ \quad\;\; CO\cdot NH\cdot NH \end{array}$ $+ (CHPh)_2N_2$. Diacetophenonecarbohydrazone behaved in a similar manner, giving *diacetophenonehydrazidicarbohydrazone*, $CO(NH\cdot N{:}CMePh)\cdot NH\cdot NH\cdot CO(NH\cdot N{:}CMePh)$, and phenyl methyl ketazine in boiling alcoholic solution, and 4-aminourazole and phenyl methyl ketazine when heated without a solvent. Benzaldehyde-δ-aminosemicarbazone was scarcely affected in boiling alcohol; prolonged boiling in toluene solution gave hydrazidicarbohydrazide and benzylideneazine: $2CHPh{:}N\cdot NH\cdot CO\cdot NH\cdot NH_2 = NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2 + (CHPh)_2N_2$. When heated a little above the melting point, the δ-aminosemicarbazone gave 4-aminourazole, hydrazine, and benzylideneazine, the former two compounds evidently resulting from the hydrazidicarbohydrazide:

$NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2 =$



$$\begin{array}{l} NH_2\cdot N\text{———}CO \\ \quad\;\; CO\cdot NH\cdot NH \end{array} + N_2H_4.$$

This work will be continued.

EXPERIMENTAL.

Carbohydrazide was prepared by Kesting's method (*Ber.*, 1924, **57**, 1323).

Diacetonecarbohydrazone (prisms from alcohol; m. p. 156°) was prepared by refluxing carbohydrazide with an excess of acetone for about 10 minutes and allowing the product to cool. Much heat was generated when the reactants were mixed (Found : N, 33·3. $C_7H_{14}ON_4$ requires N, 32·9%).

Di(methyl ethyl ketone)carbohydrazone (prismatic needles, m. p. 113°) was prepared in the same way, slightly more than 2 mols. of the ketone being used and the mixture being refluxed for only 5 minutes; the mixing of the reactants produced much heat. The almost solid product obtained on cooling was, after several hours, pressed on porous tile and then recrystallised from ether. The carbazone was readily soluble in acetone, alcohol, or water, and sparingly soluble in ether, and was rapidly hydrolysed by dilute mineral acids. This preparation was also carried out in aqueous solution, addition of potassium carbonate causing separation of the carbohydrazone (Found: N, 28·4. $C_9H_{18}ON_4$ requires N, 28·3%).

In the preparation of *diacetophenonecarbohydrazone*, the ease with which the derivatives decomposed in solution caused difficulties. 3 G. of carbohydrazide and 12 g. of acetophenone in 50 c.c. of absolute alcohol were gently heated for 1 hour; on cooling, the *carbohydrazone* (needles from aqueous alcohol; m. p. 204°) was deposited, but the yield was only 50% owing to decomposition during the working-up of the mother-liquor. The substance was sparingly soluble in cold solvents, but dissolved readily in hot water and in hot alcohol (Found: C, 69·2; H, 6·2; N, 19·2. $C_{17}H_{18}ON_4$ requires C, 69·4; H, 6·1; N, 19·0%).

3·2 G. of carbohydrazide and 4 g. of acetophenone in 50 c.c. of absolute alcohol gave, after being heated gently for 1 hour and then cooled, needles of carbohydrazide mixed with plates of *acetophenone-δ-aminosemicarbazone*. The latter compound (m. p. 188°) was isolated by dissolving out the carbohydrazide with cold water (Found: N, 29·0, 29·1. $C_9H_{12}ON_4$ requires N, 29·2%). The substance was readily soluble in hot water, alcohol, or pyridine and sparingly soluble or insoluble in other solvents.

Benzaldehyde acetophenone carbohydrazone (rhombic plates from alcohol; m. p. 160°) was obtained by refluxing 2 g. of the preceding compound and 1·5 g. of benzaldehyde in absolute alcohol for 1 hour and cooling the product. It dissolved in hot water, alcohol, benzene, and pyridine (Found: N, 19·3. $C_{16}H_{16}ON_4$ requires N, 20·0%).

Benzophenone reacted sluggishly. A solution of 1·8 g. of carbohydrazide and 3·64 g. of the ketone (1 mol.) in 10 c.c. of alcohol and 3 c.c. of water was refluxed for 7 hours, *benzophenone-δ-aminosemicarbazone*, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, being gradually deposited; after being washed with cold alcohol and with warm water, this crystallised from alcohol in glistening, diamond-shaped plates (yield, 75%), m. p. 223—224° (decomp.), which were slightly soluble in alcohol and insoluble in boiling water (Found: C, 66·2; H, 5·9; N, 22·0. $C_{14}H_{14}ON_4$ requires C, 66·1; H, 5·5; N, 22·0%).

An absolute alcoholic solution (40 c.c.) of 1·27 g. of this compound and 3 g. of benzophenone (large excess) was refluxed for 40 hours; the solution gradually became yellow, but even after this time the reaction was far from complete. On cooling, plates of the δ-aminosemicarbazone appeared followed by colourless needles of dibenzophenonecarbohydrazone. The latter, after fractional crystallisation from alcohol, melted at 222—223° (yield, 0·3 g.) (Found : C, 77·1; H, 5·5; N, 13·4. Calc. for $C_{27}H_{22}ON_4$: C, 77·5; H, 5·3; N, 13·4%) and was identical with the substance described by Borsche and Merkwitz (*loc. cit.*).

Benzaldehyde-δ-aminosemicarbazone was obtained by refluxing 5 g. of carbohydrazide and 4·5 g. of benzaldehyde in absolute alcohol for 1 hour and recrystallising from alcohol the product which separated on cooling; it formed lustrous plates, m. p. 173°, soluble in alcohol or chloroform (yield, good) (Found : N, 31·5. $C_8H_{10}ON_4$ requires N, 31·5%).

Benzilmono-δ-aminosemicarbazone, $COPh{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, was prepared by refluxing for ½ hour an absolute alcoholic solution of 5·8 g. of carbohydrazide and 13·5 g. (1 mol.) of benzil and then distilling off, during another ½ hour, most of the solvent. The almost solid mass obtained on cooling was washed with ether and recrystallised from absolute alcohol, white flakes, m. p. 172—174°, being obtained; these were slightly soluble in boiling alcohol and insoluble in benzene (Found : N, 19·2, 19·5. $C_{15}H_{14}O_2N_4$ requires N, 19·8%).

Diacetylmono-δ-aminosemicarbazone was prepared by heating on the water-bath molecular quantities of carbohydrazide and the diketone in absolute alcohol for 1 hour; the precipitate which gradually formed was collected hot and extracted twice with boiling absolute alcohol. The substance was a powder with a slightly yellow tinge, m. p. 260°, insoluble in all the usual solvents (Found : N, 35·3. $C_5H_{10}O_2N_4$ requires N, 35·4%).

An absolute alcoholic solution of acetylacetone (6 g.) and carbohydrazide (3 g.) was refluxed for 1 hour, and the solvent then evaporated. The residue, which slowly solidified, was dissolved in ether, recovered from the filtered solution, and dissolved in alcohol; slow evaporation then yielded a substance, m. p. 106—107°, which was identified as 3 : 5-dimethylpyrazole (Found : N, 29·1, 29·2. Calc. : N, 29·1%).

Thermal Decomposition of Carbohydrazones.

Dibenzaldehydecarbohydrazone.—An absolute alcoholic solution, on boiling for 24 hours, gradually became deep yellow. The solid deposited on cooling was collected, extracted with alcohol to dissolve out unchanged substance, and then recrystallised from much alcohol; the needles, m. p. 228°, thus obtained were shown to be dibenzaldehydehydrazidicarbohydrazone by comparison with an authentic specimen and by analysis (Found: N, 26·0. Calc.: N, 25·9%). The original solution from which this substance had been removed contained benzylideneazine and a little unchanged substance; separation was effected by means of ether, in which the former alone was soluble.

On heating at 205° for 1 hour, the carbohydrazone formed an amber-coloured liquid. The cold melt, on extraction with ether, left a white residue which was recrystallised from water and then proved to be 4-aminourazole (mixed m. p. test). The ethereal solution contained benzylideneazine.

Diacetophenonecarbohydrazone.—An alcoholic solution was boiled for 26 hours. It soon became yellow and deposited a white precipitate, which was collected when cold. The filtrate contained phenyl methyl ketazine. Recrystallisation of the precipitate from alcohol gave a colourless, crystalline powder, m. p. 239—240° (yellow melt), which became grey on keeping. It was *diacetophenonehydrazidicarbohydrazone* (Found: N, 24·2. $C_{18}H_{20}O_2N_6$ requires N, 23·9%) and was only slightly soluble in hot alcohol, readily soluble in hot pyridine, and insoluble in other solvents even when hot.

The carbohydrazone, on heating at 220° for 50 minutes, gave an orange-coloured and ultimately dark brown liquid, ammonia being evolved. Extraction of the cold powdered melt with ether left a white residue which, after recrystallisation from water, melted at 269—270° and was identified as 4-aminourazole by a mixed melting-point test and by analysis (Found: N, 48·4. Calc.: N, 48·3%): the yellow ethereal solution contained phenyl methyl ketazine. The yield of these products was almost quantitative.

Benzaldehyde-δ-aminosemicarbazone.—Scarcely any reaction occurred in boiling alcoholic or benzene solution. Boiling in toluene solution, however, for 31 hours effected decomposition. The white precipitate produced was collected when cold; after recrystallisation from absolute alcohol it melted at 197° and was identified as hydrazidicarbohydrazide (Stollé, *Ber.*, 1910, **43**, 2469). The toluene filtrate contained benzylideneazine.

The δ-aminosemicarbazone, on heating at 175° for 1½ hours, gave a deep yellow liquid, hydrazine, recognised by its reducing action, and ammonia being evolved. Extraction of the cold powdered melt with ether left a residue which, after recrystallisation from aqueous alcohol and then from water, melted at 270° and was identified as 4-aminourazole by comparison with an authentic specimen. The ethereal solution contained benzylideneazine.

Our thanks are expressed to Messrs. A. M. Munro, A. D. Neilson, B.Sc., and W. B. Stewart, B.Sc., for experimental assistance. We wish also to thank the Carnegie Trust for the Universities of Scotland for a research grant in aid of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

[*Received, September 23rd,* 1926.]

XIX.—*The Vapour Pressure of Water over Sulphuric Acid–Water Mixtures at* 25°.

By IVAN ROY MCHAFFIE.

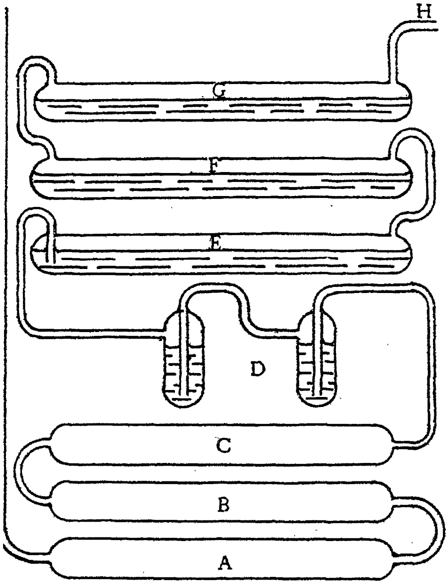
THE present investigation was carried out to test the accuracy of a method of measuring very small amounts of water vapour, present in air, employed by the author in another research. It was thought that this could be attained by measuring the vapour pressure of water over sulphuric acid–water mixtures of fairly high concentration. The results did not agree with the data relating to 25° given in the Landolt–Börnstein tables, but were in good agreement among themselves and with those of other workers. As sulphuric acid–water mixtures are frequently used for controlling the amount of water vapour present in air, the results may prove of interest.

The method of measuring small amounts of water vapour present in " permanent " gases has been described elsewhere (*J. Amer. Chem. Soc.*, 1926, 48, 1143) and is briefly as follows. The water vapour from a known volume of air is frozen out, by means of liquid air, in a condensation tube of known volume to which a mercury manometer is attached. The air is then removed from the condensation tube, still maintained at the temperature of liquid air, by mercury-diffusion vacuum pumps. The temperature of the condensation tube is then raised until all the water frozen out has been converted into vapour. The pressure of this water vapour at a known volume is then read off; hence it is possible to calculate the mass of water present.

The system of saturators is shown in Fig. 1. The tube A was filled with soda-lime, B with phosphorus pentoxide, and C with a mixture of hydrated and anhydrous oxalic acid. The bubblers, D, and the tubes, E, F, and G, contained the sulphuric acid–water mixtures. H was connected to the condensation tube, which was in turn connected to an aspirator bottle and the necessary evacuating apparatus. The volume of the portion of the apparatus containing the sulphuric acid–water mixtures was 500 c.c., half of which was filled with the mixtures. The greater amount of the spray produced in the bubblers, D, would settle out in the tubes E, F, and G; also at rates of flow varying from 1 to 4 litres per hour no change in the value of the vapour pressure at any one concentration of the mixture was observed. For these reasons, the insertion of a spray filter at the end of the saturator was considered to be unnecessary. The portion of the apparatus shown in Fig. 1 was immersed in a water thermostat maintained at 25°.

At each concentration measurements were made both with and without the tube C in the saturating system; thus equilibrium was reached with air containing both a higher and a lower concentration of water vapour than that in equilibrium with the sulphuric acid–water mixtures. At the highest concentration of sulphuric acid, each successive determination was lower than the previous one. The value given for this concentration in the following table is the first one obtained and has a probable error of 0·01 mm. The explanation of this appears to be that, with mixtures at this concentration, there is an appreciable vapour pressure of sulphuric acid as well as water vapour in the gas phase. Consequently sulphuric acid as well as water vapour would collect in the condensation tube and the pressure measured would be too low. This accumulation of sulphuric acid will not be totally removed by the evacuating pumps, during the preliminary drying of the condensation

Fig. 1.



tube, hence each reading will be lower than the preceding one. This effect cannot be due to the presence of sulphur dioxide as an impurity in the sulphuric acid, as this would tend to give too high rather than too low a result.

Results.—The readings obtained in the series of measurements at 25° are in Table I.

TABLE I.

% H_2SO_4.	$T_{asp.}$	V (c.c.).	p_b.	P_{H_2O}.	T_u.	p.	Vap. press. (mm. Hg).
65·9	15·5°	200	760·7	11·5	34·4°	15·90	1·803
65·9	15·6	275	754;5	11·5	41·0	22·15	1·789
76·0	16·3	400	747·5	12·5	17·8	5·00	0·301
76·0	17·0	600	748·4	11·0	17·8	7·33	0·295
76·0	16·3	1800	743·4	11·5	39·0	23·54	0·294
79·4	16·0	2000	745·3	12·0	31·1	13·74	0·158
83·5	17·5	5000	759·9	14·0	38·8	18·08	0·082

(The volume of the condensation tube was 23·73 c.c.)

The first column gives the proportion of sulphuric acid present in the mixtures; $T_{asp.}$ is the temperature of the aspirator; V, the number of c.c. of air passed through the apparatus; p_b, the barometric pressure; P_{H_2O}, the pressure of the water manometer attached to the aspirator; and T_u is the temperature of the condensation tube at which the pressure p, due to water vapour, was read. The last column gives the vapour pressure (in mm. Hg) calculated from the data by the expression

$$23{\cdot}73pB_{sat.}T_{asp.}/VT_uB_{asp.},$$

in which the temperatures are expressed as degrees absolute; $B_{sat.}$ is the pressure of the air within the saturator, *i.e.*, p_b corrected for P_{H_2O}; $B_{asp.}$ is the pressure of the air within the aspirator, *i.e.*, p_b corrected for P_{H_2O} and for the vapour pressure of water at the temperature $T_{asp.}$.

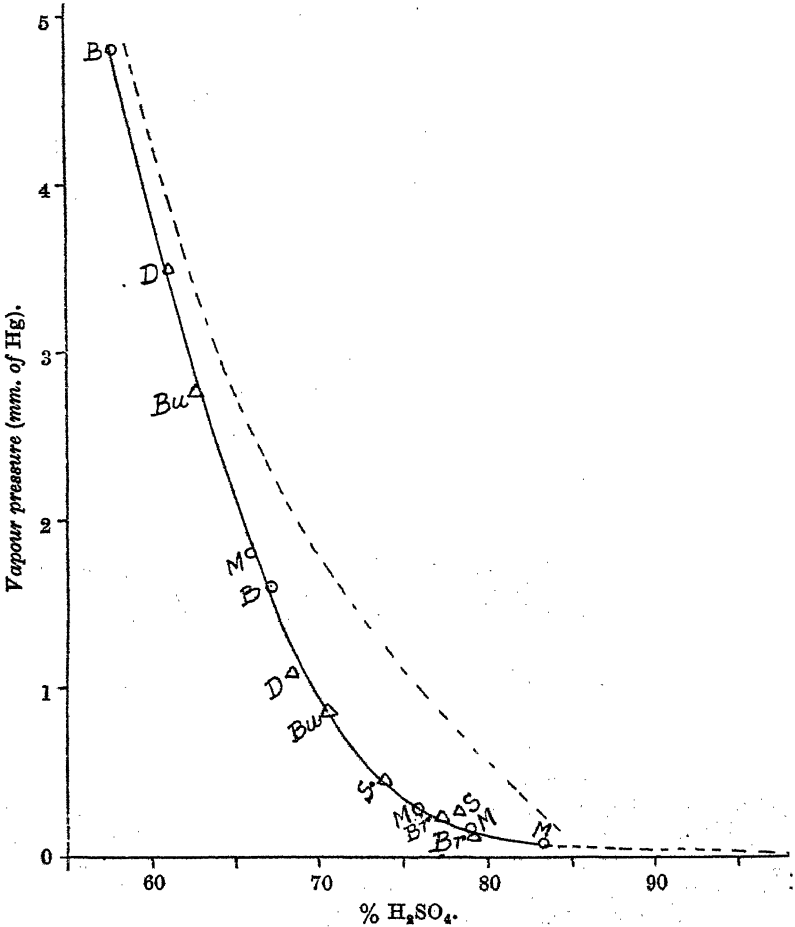
Brönsted (*Z. physikal. Chem.*, 1910, **68**, 708) (compare Lewis and Randall, "Thermodynamics," p. 331) has carried out similar measurements employing a modified tensimeter. The vapour pressures obtained by him, at the corresponding concentrations, are shown in Fig. 2.

Wilson (*Ind. Eng. Chem.*, 1921, **13**, 4, 326) has calculated the vapour pressures of these mixtures at 25° from the data of various workers obtained at 0° and 100°, by means of the equation

$$\log(r_2/r_1) = \Delta H_2(T_2 - T_1)/2{\cdot}3RT_1T_2,$$

where r_1 and r_2 are the ratios of the vapour pressures of the mixtures to those of pure water at the temperatures T_1 and T_2, and ΔH_2 is the heat absorbed when 1 mole of water is removed from the solution without change in concentration. The value of ΔH_2 used was always that for the mean between the particular T_1 and T_2 involved. These calculated values are shown in Fig. 2; the investigator upon whose data they were based is named. The values found in the present investigation are also shown. The values from the Landolt–Börnstein tables at 25° are represented by the broken curve. There is very good agreement between the calculated values of Wilson, the experimental values of Brönsted, and those of the present investigation. This would tend to show that the values obtained for the vapour pressure of water over sulphuric acid–water mixtures are

Fig. 2.



○ *Experimentally determined.* △ *Calculated by Wilson.*

B Brönsted; D Dieterici; Bu Burt; Br Briggs; S Sorel; M McHaffie.

correct, and also that the method of measuring small amounts of water vapour is trustworthy when the pressure of water vapour is as low as 0·08 mm.

Summary.

(1) The vapour pressure of water over sulphuric acid–water mixtures at 25° has been measured for mixtures containing from 66 to 84% of sulphuric acid.

(2) These results agree with the experimental values obtained by Brönsted and with those calculated by Wilson, but not with the data for 25° in the Landolt–Börnstein tables.

(3) The method employed in the present research for measuring small amounts of water present in air has been found trustworthy for pressures as low as 0·08 mm.

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XX.—*Cyclic Organo-metallic Compounds. Part III. Nitro- and Amino-derivatives of Phenoxtellurine.*

By HARRY DUGALD KEITH DREW and REUBEN WILLIAM THOMASON.

IN the thiazines and oxazines, of which methylene-blue and Meldola's blue are examples, respectively, the central ring contains the odd-valent element nitrogen, together with sulphur or oxygen. In phenoxtellurine, nitrogen is replaced by the even-valent element tellurium. Having regard, therefore, to the uncertainty which still prevails as to the distribution of bonds in the coloured salts of the first-mentioned series, it was considered desirable to investigate the properties of the amino-derivatives of phenoxtellurine (I) from the point of view of possible colour-development among their salts. For, in that event, the coloured substances of the phenoxtellurine series must of necessity consist of dimeric molecules, or must contain each an extra acid radical, in order to simulate the structures ascribed to methylene-blue and the like.

An attempt to condense 2-nitrodiphenyl ether with tellurium tetrachloride led to profound decomposition, phenolic substances being produced. Since, in addition, the condensation of amino-compounds with tellurium tetrachloride is generally unfavourable, it was decided to prepare the aminophenoxtellurines by direct nitration of phenoxtellurine, followed by reduction of the nitro-compounds. This method proved practicable.

When phenoxtellurine is treated with nitric acid, it is first quantitatively transformed by an oxidising reaction to the 10 : 10-dinitrate. Under suitable conditions, this action is then followed by nitration of the nucleus. Nitro-dinitrates, or nitro-basic-nitrates, of phenoxtellurine are thus produced; and these, on reduction by alkali bisulphite, are quantitatively transformed to nitro-derivatives of phenoxtellurine. The latter can then be reduced, by means of tin and hydrochloric acid, to the corresponding amino-derivatives.

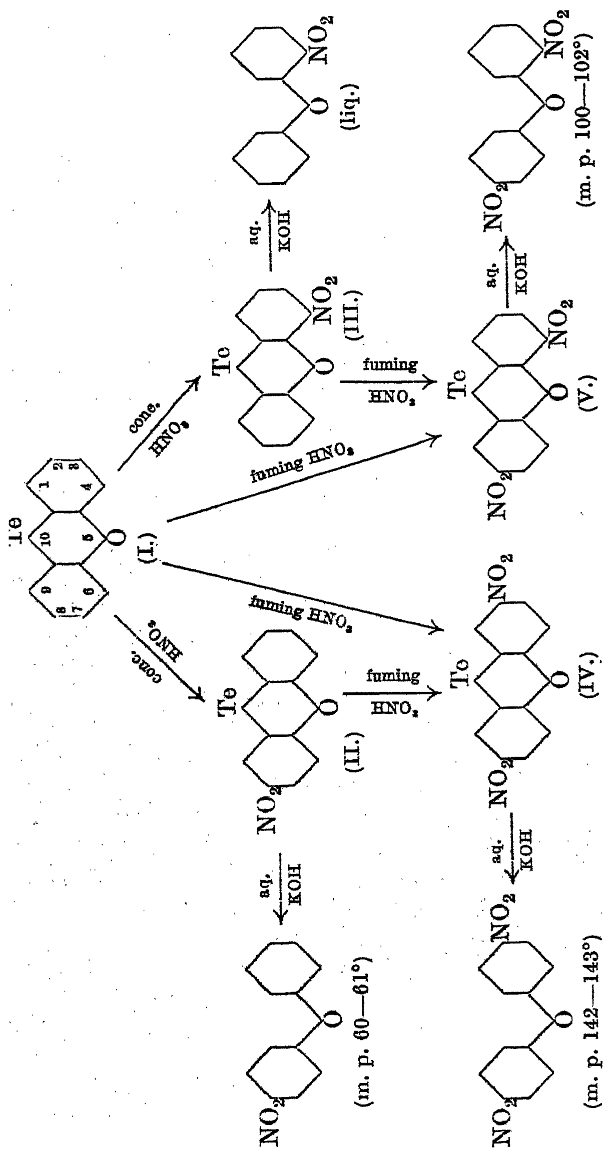
Treatment of phenoxtellurine with ordinary concentrated nitric acid (*d* 1·42) leads chiefly to the formation of mononitro-derivatives, the main product consisting of 2-*nitrophenoxtellurine* (II), the by-product being 4-*nitrophenoxtellurine* (III).

By the use of boiling fuming nitric acid, a second nitro-group is caused to enter the nucleus, and there are obtained, after reduction of the salts, 2 : 8-*dinitrophenoxtellurine* (IV) as main product and 4 : 8-*dinitrophenoxtellurine* (V) as by-product. A small proportion of 4 : 6-dinitrophenoxtellurine is doubtless also produced, but this substance has not yet been isolated.

The phenoxtellurine nucleus offers considerable resistance to further nitration, and tri- or higher nitro-derivatives were not obtained.

The nitro- and dinitro-phenoxtellurines are well-crystallised, yellow to orange-red substances, soluble in organic solvents, and possessed of considerable stability. The proof of the orientation of the nitro-groups therein was supplied in a simple manner by extending to these compounds the observation previously made, in the case of phenoxtellurine itself, that the 10 : 10-dichlorides, -dinitrates, and other similar salts are decomposed by warm aqueous potash in a manner leading to replacement of the tellurium atom by two atoms of hydrogen, potassium tellurite and the appropriate substitution product of diphenyl ether being generated in each case. Identification of the latter affords unequivocal information as to the structure of the phenoxtellurine derivative itself, except when substituents are present in positions relatively *meta*- to the ether oxygen atom (*i.e.*, in positions 1, 3, 7, or 9). So far, no such doubtful cases have been encountered. Inspection of the formulations given below will make clear the foregoing argument.

The nitrodiphenyl ethers produced from (II), (IV) and (V) by the action of potash were known crystalline substances having characteristic melting points, and the methods by which they have already been synthesised leave no doubt regarding their structure. The 2-nitrodiphenyl ether resulting from (III), however, is a liquid. The proof of the orientation of the nitro-group was therefore supplied by further nitration to (V). Confirmation of the structure of (II) was obtained by similar further nitration to (IV). The following scheme illustrates the methods employed :



The separation of the nitro-derivatives of phenoxtellurine is complicated by the existence of a series of addition compounds between the various members. Some of these occur in well-defined crystals of characteristic appearance; and repeated crystallisation from certain organic solvents fails to disrupt them, although other solvents effect complete or partial separation into the constituent substances. In the cases observed, a molecule of each of two nitro-derivatives may be combined; or two molecules of one derivative may unite with a single molecule of a second. Thus, two molecules of (IV) unite with a molecule of (II) to form a complex crystallising from acetone in orange-red prisms; whilst a molecule of (IV) unites with a molecule of (II) to form a complex separating from alcohol in yellow, hexagonal plates. Phenoxtellurine itself unites with a molecular proportion of 2-chloro-8-methylphenoxtellurine to form a remarkable *compound*, which crystallises unchanged, from petroleum or ethyl alcohol, in well-defined, yellow needles having a perfectly sharp melting point. This substance is always found associated with phenoxtellurine when the latter is prepared from ordinary (solid) diphenyl ether and tellurium tetrachloride, owing, we are of an opinion, to the presence of *p*-cresol in the material from which the diphenyl ether is made.

That these additive compounds are not the result of union between the bivalent tellurium atoms of several molecules is indicated by the fact that the corresponding complex 10 : 10-dichlorides and dinitrates, containing only quadrivalent tellurium, may in some cases be recrystallised substantially unchanged.

A point of interest emerging from the study of the nitration of phenoxtellurine is that the orienting influence of the tellurium atom, in the form of the group $>\mathrm{Te(NO_3)_2}$, on the entering nitro-groups is negligible in comparison with that of the ether oxygen atom, unless, indeed, the telluridinitrate group be considered *meta*-directive, in which case the separate influences of the two directive groups would be reinforcing. As would be expected, the entry of a second nitro-group into the phenoxtellurine ring occurs mainly, if not exclusively, in the unnitrated phenylene group.

Incidentally, the results afford confirmation of the structure of phenoxtellurine itself, since they indicate that the tellurium and oxygen atoms in that substance are attached to the phenylene groups in mutually di-*ortho*-positions.

The foregoing nitro-derivatives are readily reduced by means of tin and hydrochloric acid, 2-*amino*-, 2 : 8-*diamino*-, and 4 : 8-*diamino-phenoxtellurine* being thus produced. These substances are crystalline, stable, and appreciably soluble in water. Their hydrochlorides are readily diazotised or tetrazotised, giving yellow to red diazonium salts which may be coupled with reactive phenols, etc., to produce azo-dyes and pigments. The amines themselves have no special bactericidal action.

The action of boiling aqueous potash or soda upon the amines replaces tellurium by two atoms of hydrogen, yielding the corresponding amino-derivatives of diphenyl ether. From the latter, the amino-substituted phenoxtellurines are sharply distinguished by their instant action upon phenoxtellurine dibisulphate, mere traces of the telluride and the phenoxtellurine salt sufficing to produce, when rubbed together, the brilliant violet colour characteristic of diphenoxtellurylium salts (J., 1926, 3054).

Examination of the foregoing organic derivatives of tellurium, several of which have been carefully fractionated and repeatedly analysed, has yielded no evidence that tellurium is a complex (compare Brauner, J., 1895, **67**, 549). On the contrary, the results point to the probability that the accepted atomic weight for tellurium represents that of a single element (mixture of isotopes).

EXPERIMENTAL.

Complex By-product in the Preparation of Phenoxtellurine.—When 183 g. of tellurium tetrachloride were condensed with diphenyl ether in the manner previously described (*loc. cit.*), 178 g. of crude 10 : 10-dichlorophenoxtellurine were obtained. This, when reduced without further purification, yielded 14 g. of free tellurium, 80 g. of pure phenoxtellurine, and 20 g. of a complex by-product which closely resembled phenoxtellurine in general properties. The by-product was separated from phenoxtellurine by crystallisation from light petroleum (b. p. 40—60°), remaining in the first mother-liquor. Subsequent purification was effected from ethyl alcohol. A complete separation of these two substances is obtained with surprising ease.

The *by-product* is a compound of a molecule of phenoxtellurine with one molecule of 2(?)-chloro-8(?)-methylphenoxtellurine. It results from the presence in the diphenyl ether of a small proportion of phenyl *p*(?)-tolyl ether, which is chlorinated by tellurium tetrachloride, the product becoming transformed into 2(?)-chloro-8(?)-methylphenoxtellurine, which then unites with phenoxtellurine. It separates from ethyl or methyl alcohol, or from petroleum, in bushes of well-defined, light yellow needles with chiselled ends, and melts sharply at 59°. Conversion into the dinitrate by means of dilute nitric acid does not effect resolution of this substance into its constituents, since it is recovered unchanged on reduction of the recrystallised product. Partial separation may be obtained, however, by repeated fractionation of the 10 : 10-dichloride from chloroform. Nucleus nitration results in disintegration of the complex, nitro-derivatives of phenoxtellurine becoming isolable. In benzene solution, the compound is completely resolved into its constituents, although it is reformed when the solution is concentrated [Found : *M* (cryoscopic), 284, 287, 295. Calc., *M*, 319·8].

Mixtures of the complex substance with phenoxtellurine melt indefinitely between 59° and 79°. Removal of tellurium, by boiling with aqueous potash, gave a heavy oil which contained diphenyl ether but did not solidify. This was probably a mixture of diphenyl ether with *p*-chlorophenyl *p*-tolyl ether [Found : C, 47·05, 47·0; H, 2·9, 2·7; Cl, 5·3, 5·4; TeO, 44·9 (by diff.). $C_{25}H_{17}O_2ClTe_2$ requires C, 46·9; H, 2·65; Cl, 5·55; TeO, 44·9%]. For comparison, analyses were carried out on specimens of phenoxtellurine prepared in the same experiment (Found : C, 48·6, 48·8, 48·5; H, 2·9, 2·85, 2·8. $C_{12}H_8OTe$ requires C, 48·7; H, 2·7%).

Nitration of Phenoxtellurine.—(1) *Preparation of mononitrophenoxtellurines.* Powdered phenoxtellurine (4·5 g.) was added slowly to 70 c.c. of nitric acid (*d* 1·42), and the orange-red solution obtained after 10 minutes' boiling yielded, after 2 days, opaque, white needles (5·7 g., after being dried over soda-lime). The mother-liquor, concentrated on the water-bath, yielded further solid (0·9 g.) which, on reduction, gave chiefly 2 : 8-dinitrophenoxtellurine.

The main crop (5·7 g. above), when reduced by 30 c.c. of water and 5·7 g. of potassium metabisulphite, was transformed into a dark paste. The yellow ethereal extract of this, when allowed to evaporate on a wide surface, left yellow needles (A) surrounded by orange-red flakes (B). These two products were separated mechanically and each was crystallised from acetone. The orange-red flakes (B) gave slender, yellow crystals of 2 : 8-dinitrophenoxtellurine, together with massive, red prisms melting gradually from 145° to 220°. The latter substance was a *compound* containing two molecular proportions of 2 : 8-dinitrophenoxtellurine and one proportion of 2-nitrophenoxtellurine, into which it was separated by fractionation from ethyl alcohol (Found : N, 6·0. $C_{36}H_{19}O_{13}N_5Te_3$ requires N, 6·3%). From acetone, the complex could be recrystallised almost unchanged.

The yellow needles (A) gave a first crop of crystals, part of which dissolved more readily than the remainder in hot ethyl alcohol. The soluble portion separated from alcohol in silky, bright yellow needles of 2-*nitrophenoxtellurine* (II), m. p. 129° (Found: C, 42·2; H, 2·25; N, 4·25. $C_{12}H_7O_3NTe$ requires C, 42·3; H, 2·05; N, 4·1%). The less soluble portion separated from hot alcohol in glistening, bright yellow spangles, consisting of thin, hexagonal prisms. This substance was a *compound* of 2 : 8-dinitro- and 2-nitro-phenoxtellurines in molecular proportion (Found : N, 5·7. $C_{24}H_{13}O_8N_3Te_2$ requires N, 5·8%). The complex could be recrystallised unchanged from alcohol, but was partly disrupted by acetone. It melted gradually between 145° and 185°.

The acetone mother-liquor from A, allowed to evaporate very slowly, gave small, yellow needles of impure 2-nitrophenoxtellurine, together with massive, lemon-yellow prisms. The prisms, sorted out by hand and recrystallised from ethyl alcohol, gave pale lemon-yellow prisms or needles of 4-*nitrophenoxtellurine* (III), m. p. 104° (Found: C, 42·4; H, 2·2; N, 4·2%).

(2) *Preparation of dinitrophenoxtellurines.* Powdered phenoxtellurine (4·3 g.) was added gradually to 25 c.c. of nitric acid (*d* 1·50), cooled in ice and salt. The mixture was then heated on a water-bath during ½ hour. The cooled solution was precipitated by addition of water and the white solid was removed and recrystallised from boiling nitric acid (*d* 1·42). The first crop (3·9 g.), when crystallised again from nitric acid, gave large, colourless, serrated needles (2·9 g.) which, on reduction with aqueous potassium metabisulphite, yielded pure 2 : 8-*dinitrophenoxtellurine* (IV), m. p. 228°. This substance crystallised from acetone in large, hexagonal, orange prisms, or from ethyl alcohol in smaller, yellow prisms. It was more sparingly soluble in organic solvents than the foregoing mononitrophenoxtellurines (Found: C, 37·9; H, 1·85; N, 7·3. $C_{12}H_6O_5N_2Te$ requires C, 37·4; H, 1·55; N, 7·3%).

The nitric acid mother-liquor from the above first crop was diluted with water and the white precipitate (4·2 g.) was boiled with 20 c.c. of fuming nitric acid during 2 hours. Precipitation by water and crystallisation of the precipitate from concentrated nitric acid gave a further crop of the above serrated needles. The nitric acid mother-liquor from this crop slowly deposited a second substance in minute, white rods. This, after recrystallisation in a similar manner from concentrated nitric acid, yielded, on reduction with aqueous potassium metabisulphite, pure 4 : 8-*dinitrophenoxtellurine* (V), m. p. 197—198°. This substance crystallised from benzene in long, thin, golden, lath-like needles containing $\frac{1}{2}C_6H_6$ (Found: loss of benzene at 100°, 9·2. Calc., 9·3%). The benzene was slowly lost in the air, the dinitro-compound remaining as a salmon-red, crystalline powder (Found: C, 37·0; H, 1·9; N, 7·3%). The substance separated from ethyl alcohol in minute, red crystals. It was generally only sparingly soluble in organic solvents.

Although the basic nitrate of 4 : 8-dinitrophenoxtellurine is much less easily soluble in nitric acid than is the dinitrate of 2 : 8-dinitrophenoxtellurine, the former tends to remain in supersaturated solution while the latter crystallises readily.

Many other experiments on the nitration of phenoxtellurine with nitric acid under a variety of conditions led to the conclusion that the reaction cannot be controlled so as to produce mononitro-compounds only, lesser proportions of dinitro-compounds invariably being present. On the other hand, conditions are readily chosen in which only dinitro-compounds are produced. Fuming nitric acid, at atmospheric pressure, seems to be incapable of introducing more than two nitro-groups into the phenoxtellurine nucleus. Nitration in presence of auxiliary acids has not yet been tried.

Nitration of 2-Nitrophenoxtellurine.—A solution of 2-nitrophenoxtellurine in fuming nitric acid was boiled during 2½ hours. Separation of the products in the manner already described yielded crystals which, on reduction, gave pure 2 : 8-dinitrophenoxtellurine. The mother-liquor contained a substance which furnished, on reduction, a mixture of 2 : 8- and 4 : 8-dinitrophenoxtellurine. The latter, present only in very small proportion, was not isolated but was characterised by its colour change on crystallisation from benzene and exposure of the crystals to air.

Nitration of 4-Nitrophenoxtellurine.—Finely powdered 4-nitrophenoxtellurine (0·4 g.) was added slowly to cold fuming nitric acid (5 c.c.). The solution was boiled during 2 hours, and water was then added until a turbidity appeared. The white solid which subsequently separated was reduced with aqueous potassium metabisulphite, furnishing, after crystallisation from benzene, pure 4 : 8-dinitrophenoxtellurine (V), m. p. 198°, in 60% yield. The mother-liquor contained another nitro-compound, probably 4 : 6-dinitrophenoxtellurine, but the proportion was too small to allow of its isolation.

Conversion of Nitro-derivatives of Phenoxtellurine into Nitro-derivatives of Diphenyl Ether.—2-Nitrophenoxtellurine was converted into its dinitrate by means of nitric acid, and the crystals were boiled for a few minutes with 50% aqueous potash. Extraction by a mixture of ether and benzene furnished a solid which, after one crystallisation from ethyl alcohol, gave 4-nitrodiphenyl ether in very pale yellowish-white, flat plates, m. p. 60—61°.

4-Nitrophenoxtellurine was converted into its 10 : 10-*dibromide* (pale yellow crystals, melting and decomposing at 302°), which was then boiled with 30% aqueous potash. Extraction with ether gave *o*-nitrodiphenyl ether, a pleasant-smelling oil which did not solidify on keeping.

2 : 8-Dinitrophenoxtellurine, similarly converted into its dinitrate and boiled with 30% aqueous potash, yielded a solid which, after one crystallisation from alcohol, gave pale yellowish-white needles of 4 : 4′-dinitrodiphenyl ether, m. p. 142—143°.

4 : 8-Dinitrophenoxtellurine was converted into the basic nitrate,

and the latter boiled with 50% aqueous potash for a few minutes; the mixture was diluted with an equal bulk of water and then further heated at 100° for an hour. Extraction with much benzene gave 2 : 4′-dinitrodiphenyl ether, large, brittle, glassy, brownish prisms, m. p. 100—102°, from alcohol.

Amino-derivatives of Phenoxtellurine.—2-Aminophenoxtellurine. Finely powdered 2-nitrophenoxtellurine (2 g.) was heated on a water-bath during several hours with a large excess of tin and concentrated hydrochloric acid, until the yellow colour of the nitro-compound had disappeared. After filtration, the solid and filtrate were treated separately with cold caustic soda solution, and the liberated amine was extracted with chloroform in a Soxhlet apparatus. The amine was converted into the hydrochloride, which crystallised from water in small, very pale yellow needles. The addition of caustic soda to this solid gave 2-*aminophenoxtellurine*, which crystallised from aqueous alcohol in pinkish-white needles, m. p. 157° (Found: N, 4·65. $C_{12}H_9ONTe$ requires N, 4·5%). Proof of orientation of this amine was shown by boiling it with aqueous potash, 4-aminodiphenyl ether (colourless needles from alcohol; m. p. 84°) being obtained.

By diazotising 2-aminophenoxtellurine at 0°, a pale yellow solution was obtained; and this, on coupling with alkaline β-naphthol, gave an insoluble, red azo-dye.

2 : 8-*Diaminophenoxtellurine.*—Finely ground 2 : 8-dinitrophenoxtellurine (3·8 g.) was heated with tin and concentrated hydrochloric acid on the water-bath, the red powder gradually becoming yellow; it was necessary to decant the clear liquid occasionally and grind the solid. The sparingly soluble hydrochloride of the amine was collected and treated with caustic soda. The amine thus formed was filtered off and extracted with chloroform, the cooled extract yielding 2 : 8-*diaminophenoxtellurine*, which crystallised from alcohol in lemon-yellow needles, m. p. 198° (Found: C, 44·3; H, 3·05; N, 8·6. $C_{12}H_{10}ON_2Te$ requires C, 44·2; H, 3·05; N, 8·6%). This diamine is slightly soluble in water and yields a hydrochloride which crystallises from hot water in long, yellow needles. Tetrazotisation causes the formation of a blood-red solution which yields an insoluble red azo-dye with alkaline β-naphthol.

4 : 8-*Diaminophenoxtellurine.* When 4 : 8-dinitrophenoxtellurine was similarly treated with tin and hydrochloric acid, the reduction proceeded much more rapidly. After the orange colour had disappeared, the hydrochloride was separated and crystallised from water. The action of caustic soda liberated 4 : 8-*diaminophenoxtellurine*, which crystallised from aqueous alcohol or water in faintly yellow, feathery needles or mica-like plates, m. p. 156° (Found:

C, 44·15; H, 3·0; N, 8·65%). On tetrazotisation, the diamine yielded a bright red diazonium chloride, which formed a red azo-dye with alkaline β-naphthol.

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XXI.—*Anticathodic Luminescence of some Organic Substances.*

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WHEN organic substances are cooled and bombarded with cathode rays there is very frequently an emission of light of greater or less intensity. This phenomenon was first extensively studied by Goldstein (*Verh. deut. physikal. Ges.*, 1904, 6, 156). Later a study was made by O. Fischer (*Z. wiss. Phot.*, 1908, 6, 305) of a number of substances which gave discontinuous spectra. From his work, it is evident that there is usually some degree of regularity in the position of the bands given by each substance, and Baly (*Phil. Mag.*, 1915, 29, 223) and Henri ("Etudes de Photochimie," 1919) have both found support for their theories with regard to the relationship of infra-red and ultra-violet spectra from the positions of the anticathodic luminescence bands.*

The present work was undertaken in the hope that some further information might be gained as to the origin and significance of the anticathodic glow. Visual observations were made of a large number of organic substances, but in the great majority of cases the glow was too feeble to admit of photography, and also it was often continuous in character. Goldstein distinguished three different spectra which it was possible for one substance to exhibit, *viz.*, an initial spectrum, the chief spectrum, and a solution spectrum. The present investigation has been confined to pure substances, so that it is not concerned with solution spectra. All the substances examined showed a partial loss of luminescent power after a few minutes or even seconds of bombardment. This was due in part to the fading of the initial spectrum. Partial recovery sometimes occurred after an interval of rest, but some of the loss of luminescent power was due to a surface decomposition of the material. The initial spectrum was usually of greatest interest, as it sometimes consisted of distinct, bright bands; these gradually diffused themselves into a continuous spectrum—the chief spectrum of Goldstein. A phosphorescence lasting often for a minute or more was frequently seen on stopping the bombardment. This sometimes gave a spectrum which consisted of the same bands as were observable during the bombardment and, like the initial spectrum, decreased after a period of excitation.

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* These spectra have usually been termed cathodo-luminescence, but are produced when the materials act as anticathodes in a discharge tube, and so the term anticathodic luminescence would seem to be more fitting.

A discharge tube similar in type to that used by Fischer was employed, and liquid air was used for cooling. In some cases, the glow, and likewise the phosphorescence, was stronger at temperatures higher than that of liquid air. There was also the disadvantage that the liquid exhibited several absorption bands across the usual range of the anticathodic luminescence spectrum, but, on the other hand, it enabled rather volatile substances to be examined. A small silica vacuum cup with an unsilvered patch held the liquid air into which the end of the discharge tube dipped. The spectrograph was a two-prism glass instrument giving a bright visible spectrum about 5 cm. long.

The materials examined fall into four classes, giving, respectively, (1) little or no glow, (2) a continuous spectrum only, although often of a distinctive hue, (3) a glow identifiable with the fluorescence spectrum, and (4) a distinctive banded spectrum.

(1) Those giving little or no spectrum include fully saturated compounds, nitro-compounds, strongly coloured substances, aldehydes, etc.; the following substances were found to belong to this class: hexane, paraffin wax, oleic acid, dipentene, bisdiphenylene-ethylene, carbon tetrachloride, hexachloroethane, nitrobenzene, *m*-nitroanisole, *o*-nitrophenol, benzaldehyde, cinnamaldehyde, quinone, quinol, 1 : 2-naphthaquinone, diphenyl ether, acridone, azobenzene, rosaniline, *p*-anisidine, benzaldoxime, and quinoline.

(2) A continuous spectrum was furnished by the following substances. The glow was most often blue or violet to the naked eye. Other colours are recorded in brackets after the substance. Stilbene, tolane, phthalic acid, terephthalic acid, *p*-hydroxybenzoic acid, phenol (green), *p*-cresol (green), fluorenone (green), coumarin, benzonitrile, *p*-chloroaniline, *p*-chlorobenzaldehyde, ethyl *p*-aminobenzoate (white), acridine (green), phenazone, sodium naphthionate, methyl propyl ketone, *s*- and *as*-diphenylurea, acenaphthenequinone (orange), 9 : 10-dinitroanthracene (yellow), benzanilide.

(3) In the following instances the glow was similar to the usual fluorescence spectrum: Anthracene, 1 : 2-benzanthracene, 9-phenylanthracene, 9 : 10-dichloro- and -dibromo-anthracenes, carbazole, aniline, α- and β-naphthylamines, diphenylamine, *p*-phenylenediamine. Probably also the blue glow given by a number of substances in the previous list is a continuation of the ultra-violet

fluorescence reaching up into the visible region under strong stimulation.

(4) Of those substances which gave banded spectra, only a minority have been completely investigated by photography. In other instances, the spectrum was too weak. Characteristic of all the stronger spectra was a well-marked head making an abrupt termination to the end of shorter wave-length. This head was often in the green region and never below the greenish-blue, but was sometimes in the red. The bands appeared on a bright continuous background, and to the blue side of the first head there was often a continuous spectrum also, although distinctly weaker.

The substances which have been photographed were chiefly aromatic hydrocarbons and naphthalene derivatives. Some of these have already been fully examined by Fischer, but others are now dealt with.

Toluene gave a continuous spectrum throughout the visible, but strongest between 4200 and 4800 Å. There was a strong band at 1/λ 2090, and others at 2193, 2151, and 1816.

p-*Cymene* glowed green and showed two distinct bands at 1/λ 2153 and 2083, and faint ones at 2222 and 1942, thus giving a series having an interval of about 70.

m-*Xylene* gave a spectrum less intense and much more diffuse than those of its isomerides (Fischer, *loc. cit.*). The same is true also of the absorption and fluorescence spectra. It showed, however, one very definite head at about 1/λ 2105 and signs of a second at 2224.

Mesitylene had five or six bands beginning in the bluish-green region, but fading quickly; it was not successfully photographed.

Naphthalene. The spectrum was in substantial agreement with Fischer's figures, but the first band on commencing excitation showed a doubling, which, however, was lost after a short time. The two heads were at 1/λ 1854 and 1850.

Tetrahydronaphthalene possessed a remarkably strong luminescence. Edge of spectrum, 1/λ 2123. Very strong double band, 2096 and 2075; also bands at about 2018, 1976, 1925, 1862, 1805, and 1715. The band 1925 is strong; the others are rather diffuse.

Octahydroanthracene also gave an intense spectrum starting at 2044 and having a strong double band at 1/λ 2043 and 2027. There were diffuse bands at about 1907, 1862, 1740, and a continuous region to the limit of the visible red.

Acenaphthene glowed orange-red and gave a number of bands which were fairly sharp on the blue edge in the case of the stronger ones. Positions, 1/λ 1767, 1748, 1717, 1691, 1629—1605, 1558. The fourth and the last are the strongest.

Triphenylmethane had a head at 1/λ 1930—1912 at the beginning of a continuous region extending to the limit of the red, with another diffuse maximum about 1750.

Diphenylmethane gave a yellowish-green glow which, however, was difficult to photograph. A change appeared to take place, the material giving a white solid of higher melting point.

α-*Methylnaphthalene* gave three strong bands, 1/λ 1825, 1690, 1556, and a faint one about 1640. There was also a strong continuous emission from the violet to 5000 Å.

β-*Methylnaphthalene* showed two strong heads, 1/λ 1657 and 1521, the former being particularly intense. There appeared to be a number of lesser maxima about 1815, 1780, 1604, and 1568, as well as a continuous region from the violet to 5000 Å.

α-*Naphthol* glowed red but soon fatigued, and showed only very indefinite maxima at about 1/λ 1664 and 1567.

β-*Naphthol* glowed less strongly than the last and more yellow in colour. The methyl ether showed bands at 1/λ 1757 and 1658.

Other substances which gave banded spectra were hexaethylbenzene, styrene, fluorene, phenylfluorene, chlorobenzene, *p*-dichlorobenzene, α-chloronaphthalene, hexachlorobenzene, ψ-cuminol, diphenylcarbinol, quinol dimethyl ether, anthraquinone, phenanthraquinone, *p*-tolyl methyl ether, 1 : 5-dihydroxynaphthalene, and α-naphthyl methyl ether.

Discussion of Results.

On comparing the anticathodic luminescence spectra with the Tesla-luminescence, it is apparent that what has been noted and described as the Tesla green glow (Marsh, *Phil. Mag.*, 1925, **49**, 971), from its usual appearance in a number of vapours, is substantially identical with the anticathodic glow of the solids, although there may be a strong anticathodic glow and yet little sign of emission from the vapour, *e.g.*, in naphthalene. In the cooled solids, the glow usually extends further towards the red than was found with the Tesla glow, and is stronger; and, as would be expected, the bands are displaced a little towards the region of greater wavelengths. This shift amounts to 1/λ 40 or more.

The position of the abrupt blue end of the anticathodic glow varies in a manner parallel with the variation of the absorption and fluorescence regions of the substance. There is a fairly definite frequency interval between the fluorescence and anticathodic glow regions. This is seen in the accompanying table, and must indicate a more or less fixed energy difference between two levels of activation common to all the substances.

TABLE I.

Substance.	Absorption-fluorescence boundary.	Anticathodic luminescence (short λ end).	Difference.
Toluene	3749	2151	1598
o-Xylene	3731	2099	1632
m-Xylene	3759	2108	1651
p-Xylene	3741	2131	1610
p-Cymene	3690	2153	1537
Tetrahydronaphthalene	3678	2085	1593
Octahydroanthracene	3528	2035	1493
Naphthalene	3245	1840	1405
Acenaphthene	3264	1767	1497
α-Methylnaphthalene	3333	1825	1508
β-Methylnaphthalene	3333	1815	1518
Triphenylmethane	3546	1921	1625
Styrene	3475	1912	1563

With the exception of naphthalene, the differences found do not vary by more than 10%.

The atomic-group spectra found in the infra-red show bands to a large extent independent of the exact molecular structure from which they originate, and although absorption bands of this series have been traced as far down as 0·606μ, they seem to have no direct connexion with the anticathodic bands. The above-noted interval between absorption or fluorescence and the anticathodic spectra, on the other hand, tends to show that the origin of the last is similar to that of the first two. Moreover, between the absorption, fluorescence, and anticathodic luminescence there is a distinctly traceable resemblance in structural detail. The clearest example of this is in *p*-xylene. Mies (*Z. wiss. Phot.*, 1909, 7, 357) has measured 16 absorption bands divisible into two series giving an average interval 1/λ 79·5, and the anticathodic luminescence (Fischer) shows ten bands in two series with an average interval of 81·2. The Tesla-luminescence bands are again divisible into two series with an average interval of 81.

It must be admitted that not all the anticathodic luminescence spectra examined show a degree of regularity approaching that of *p*-xylene, but in most instances some sort of order is apparent in the case of the stronger heads, which, however, are often so diffuse that the accuracy of measurement scarcely justifies much deduction. In the case of naphthalene the three strongest bands appear at 1/λ 1840, 1694, and 1542, giving intervals of 146 and 152, similar in size to those found in other naphthalene spectra (Marsh, *Phil. Mag.*, 1925, 49, 971; László, *Z. physikal. Chem.*, 1925, **118**, 369). The four strongest bands of acenaphthene (1558, 1617, 1691, and 1748) show intervals of 133 and 131. α- and β-Methylnaphthalenes give spectra resembling that of the parent hydrocarbon, but more diffuse and having an average interval of about 135. The bands in the case of the β-derivative have undergone a shift towards the red region. In *p*-cymene, there is a regularity at intervals of 70 units, and so on. For a discussion of the significance of these intervals reference may be made to previous papers by the author (*Phil. Mag.*, 1925, 49, 1206; J., 1926, 724).

Fischer found three equally-spaced broad bands between 4100 and 4700 Å. in very many of the substances he examined. Like several other workers, he has not recognised these as due to traces of anthracene. They belong to the ordinary fluorescence spectrum of this substance. On bombarding anthracene itself, they are produced, but not with particularly great intensity, and decomposition is rather rapid, but a mere trace of anthracene in another substance will give rise to them. The chemicals in which Fischer found these bands now ascribed to anthracene were: Naphthalene, β-naphthonitrile, α- and β-acetonaphthalide, α- and β-naphthol, x- and β-naphthylamine, dibenzyl, and phenanthrene.

It is worthy of note that benzaldehyde was found not to give an anticathodic glow. Most substances capable of light emission will give a fluorescence, a Tesla-luminescence, and an anticathodic glow. The Tesla glow of benzaldehyde, however, appears to be the only emission of which it is capable. This glow seems to bear some relation to the fluorescence, inasmuch as it occurs in the same position as the extra absorption band developed in concentrated sulphuric acid solutions, which, according to Baly, usually occurs in the fluorescence zone of the alcoholic solutions.

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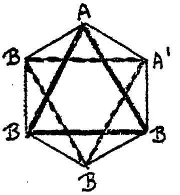
[*Received, June 28th,* 1926.]

XXII.—*The Isomerism of Molybdenyl Monochloride.*

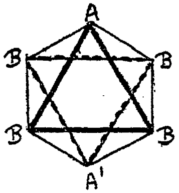
By WILLIAM WARDLAW and ROBERT LOUIS WORMELL.

THE results of conductivity measurements have shown that a wide range of chemical compounds has a co-ordination number of six. In the cases of cobalt, iron, chromium, rhodium, and iridium, of which the derivatives exhibit geometrical isomerism and are capable of resolution into optically active components, it has been proved that the six associating units have an octahedral distribution round the central metallic atom.

Determinations of the ionisation of a number of compounds of tervalent molybdenum have indicated a co-ordination number of six, but so far there is no evidence as to the spatial distribution of the associating units. Three arrangements must be considered—the hexagon, the triangular prism, and the regular octahedron. Either of the first two configurations demands three isomeric forms for the complex $[MAA'B_4]$, but if the units are situated at the vertices of a regular octahedron then only two stereoisomerides are possible, *viz.*, *cis-* and *trans-* :



Cis-.



Trans-.

This important test has been applied to the co-ordination compound $[MoOCl,4H_2O]$, and two isomeric forms have been isolated to which *cis-* and *trans-*configurations have been assigned. This has furnished the first indication that molybdenum can give rise to co-ordination compounds in accordance with Werner's view of their sixfold structure.

EXPERIMENTAL.

Brown Molybdenyl Monochloride.—In a previous communication (J., 1924, **125**, 2370), it was shown that when a solution of molybdenum trioxide in hydrochloric acid is reduced electrolytically to the tervalent condition, concentrated to small bulk, re-electrolysed, and the resulting reddish-brown liquid poured into air-free acetone, a buff-coloured solid separates, the analysis of which corresponds to MoOCl with approximately $4H_2O$. It was later found that, on precipitating the oxychloride from a solution with a molybdenum content only one-fourth of that indicated in our paper (*loc. cit.*), the dried product gave an analysis in close accordance with that demanded by $MoOCl,4H_2O$ (Found: Mo, 44·1; Cl, 16·3; Mo : Cl = 1 : 1. $MoOCl,4H_2O$ requires Mo, 43·7; Cl, 16·2%).

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water :

G. of $MoOCl,4H_2O$ per 10 g. of water	0·2531	0·1669	0·1682
" Apparent " mol. wt.	191·3	185·6	186·1

The molecular weight for the non-ionised substance $[MoOCl,4H_2O]$ is 219·5. Here, as in the case of many co-ordination compounds, the substance has apparently undergone hydrolysis whereby the

$$[MoOCl,4H_2O] + H_2O = [MoO,5H_2O]Cl \rightleftharpoons [MoO,5H_2O]^{\cdot} + Cl'.$$

co-ordinated chlorine atom is replaced by a molecule of solvent; this hydrolysis produces a binary electrolyte, the existence of which would influence the molecular-weight determinations in the foregoing manner. This progressive hydrolysis is also shown by the results of conductivity measurements at 1°.

For $v = 4$ litres per mole:

μ	33·7	38·1	39·9	40·8	44·8	46·8	50·8
Time (mins.)	4	8	12	15	43	80	220

For $v = 25$ litres per mole:

μ	33·0	38·9	42·9	45·7	48·2	49·7	51·1	52·3	53·3	65·2
Time (mins.)	2	3	4	5	6	7	8	9	10	40

In more dilute solutions, the rate of hydrolysis increased.

Now, for a binary electrolyte, *e.g.*, potassium chloride, the data at 1° are:

v (litres per mole)	8	16	32
μ	72·2	75·2	77·3

and the fact that the above conductivities alter with time and approach the value for a binary electrolyte, combined with the molecular-weight determinations, indicates that the brown oxychloride is not a binary electrolyte and that it is correctly formulated as the co-ordination compound [$MoOCl,4H_2O$].

On the assumption that the six associating units are octahedrally distributed round the molybdenum atom, two isomeric oxychlorides should exist corresponding to *cis*- and *trans*-isomerism. The existence of this second molybdenyl chloride seems to be indicated from the fact that a solution of tervalent molybdenum in hydrochloric acid may be either reddish-brown or green, depending on the acid concentration. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146, 173) prepared the former solution by electrolytic reduction of molybdenum trioxide dissolved in 9*N*-hydrochloric acid, and the green solution was obtained when the acid used was 4—2·7*N*. Whilst the red solutions, having a content of 3·67% of molybdenum trioxide in the original solution and after complete reduction to the Mo^{III} stage, never exceed a static potential of $E_h = +0·12$ volt at 24—26°, and are stable even in air, the green solutions under similar conditions attain potentials of $-0·18$ volt and are readily oxidised by air and water—especially in contact with platinum—with evolution of hydrogen. A further difference between the two solutions was found by Bredig and Michel (*Z. physikal. Chem.*, 1922, **100**, 136), *viz.*, that the green solution reduces perchloric acid 2000 times as quickly as the red. It was anticipated, therefore, that a green molybdenyl chloride would be isolated from the green solution of tervalent molybdenum and that it would be characterised by much greater reactivity than its brown isomeride. Such an oxychloride was obtained as follows.

Green Molybdenyl Monochloride.—A solution of molybdenum trioxide (60 g.) in 390 c.c. of hydrochloric acid (*d* 1·16) was diluted to 500 c.c., electrolysed for 4 hours in a diaphragm cell and concentrated at 50° under diminished pressure to 250 c.c. This concentrated solution, in which the molybdenum was quinquevalent, was then re-electrolysed. On prolonged electrolysis, the solution became green and the concentration of "free" acid diminished. At this stage, a portion of the solution, on being poured into acetone, gave a bluish-green precipitate, a typical hydrolysed product. The cell was now cooled in ice, and the cathode liquid forced by pressure of carbon dioxide into an equal volume of ice-cold 10*N*-hydrochloric acid. The olive-green solution thus produced was poured into air-free acetone and a green solid then separated in excellent yield. It was filtered off, washed with acetone, and dried in a vacuum desiccator. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded.

The valency of the molybdenum in this compound was determined as in the case of the brown oxychloride, and was found to be three.

Analysis.—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The chloride in the filtrate and washings was estimated as silver chloride (Found: Mo, 46·2, 45·8; Cl, 17·2, 17·0; Mo : Cl = 1 : 1·01, 1 : 1·01. $MoOCl,3H_2O$ requires Mo, 47·6; $MoOCl,4H_2O$ requires Mo, 43·7%). As the solid had been dried in an evacuated desiccator, it is probable that its normal composition is $MoOCl,4H_2O$. These results show a close resemblance to those recorded (J., 1924, **125**, 2370) for the brown oxychloride isolated under similar conditions.

Properties and Reactions of Green Molybdenyl Chloride.—The freshly-precipitated solid is green, but on drying it becomes greyish-green. On exposure to the air, it darkens in colour and hydrolyses. It is more readily soluble in water and in concentrated hydrochloric acid than its brown isomeride, but is insoluble in alcohol. It has similar reducing properties to the brown oxychloride, but is much more reactive.

Molecular-weight Determinations.—The molecular weight was determined by depression of the freezing point of air-free water:

G. of $MoOCl,4H_2O$ per 10 g. of water ...	0·9774	1·0146	0·2302
"Apparent" mol. wt.	191·4	196·5	161·7

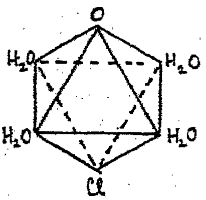
If the green solid were an ionisation isomeride of the brown oxychloride, it would be formulated as [MoO]Cl,$4H_2O$, in which case its apparent molecular weight would be 109·75 for complete ionisation. The above results indicate that green molybdenyl chloride should be formulated as [MoOCl,$4H_2O$] and that it is much more rapidly hydrolysed than its isomeride. The results of conductivity measurements are open to the objection that during their determination the green solution undergoes slow oxidation by decomposition of the water, in the presence of the electrodes, with evolution of hydrogen. Nevertheless, in spite of the possibility of this side-reaction, the results obtained afford confirmatory evidence that the green solid has the co-ordination formula [MoOCl,$4H_2O$]:

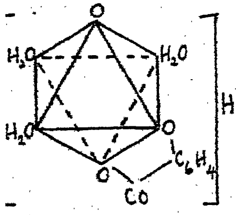
At 1° for $v = 5·7$ litres per mole:

μ	42·77	48·9	50·6	51·9	53·1	53·6
Time (mins.)	1	3	4	5	6	7

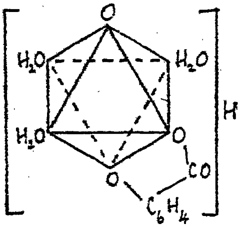
On the other hand, with concentrated solutions such as $v = 0·5$ litre per mole, the value of μ after one hour was only 19·7. These and other determinations indicated that by continuous hydrolysis a binary electrolyte was being formed, but that initially the compound was a non-electrolyte.

The Stereoisomerism of the Oxychlorides.—The existence of two isomeric co-ordination compounds, MoOCl,$4H_2O$, having been established, it is necessary now to assign to them *cis*- and *trans*-configurations. This has been made possible by a study of reactions in which the salicylate group has functioned as an unsymmetrical chelate group. Theoretical considerations indicate that by the interaction of monosodium salicylate, $NaH[O·C_6H_4·CO_2]$, and the *trans*-molybdenyl chloride, two products may be produced:



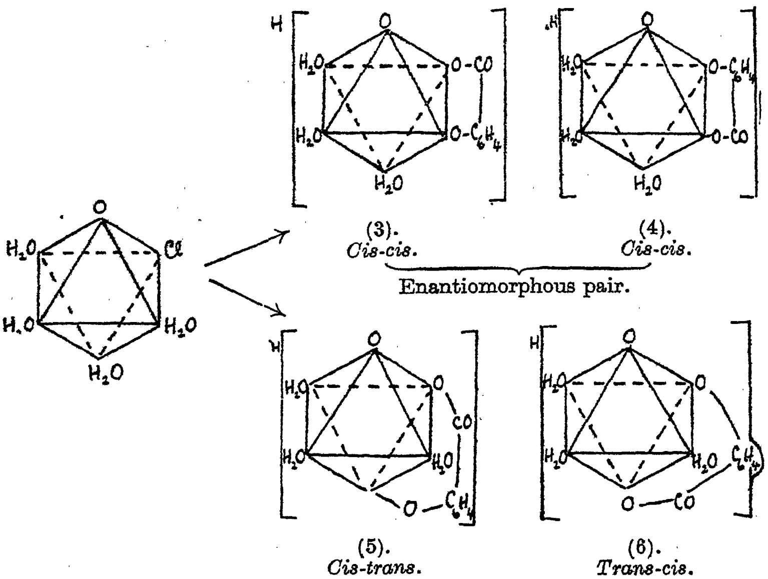


(1).
Trans-cis.



(2).
Cis-trans.

By interaction of monosodium salicylate and *cis*-molybdenyl chloride, on the other hand, four products are theoretically possible, of which two (Nos. 3 and 4) are enantiomorphs:

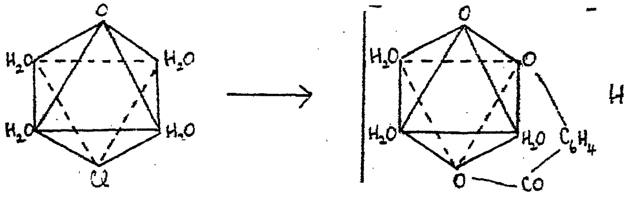


(3). *Cis-cis.* (4). *Cis-cis.*

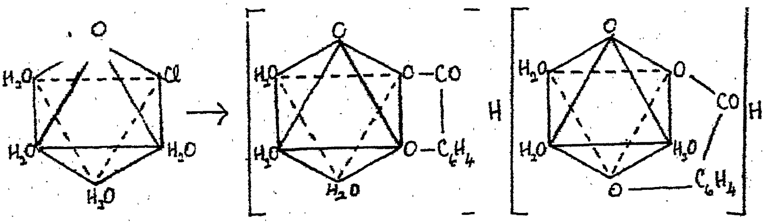
Enantiomorphous pair.

(5). *Cis-trans.* (6). *Trans-cis.*

However, these different isomerides would be produced only on the assumption that the oxygen of the phenolic hydroxyl group and that of the carboxyl group equally well replace the chlorine unit in the co-ordination sphere. Experiment shows that this is not so. When the green oxychloride reacts with monosodium salicylate a precipitation of green molybdenyl salicylate takes place. This should theoretically be a mixture of isomerides (1) and (2). The interaction of the brown oxychloride and monosodium salicylate results in the formation of an insoluble brick-red substance, together with an intensely red-coloured liquid, which continuously deposits the insoluble product on keeping. Since (1) and (2) are identical with (5) and (6), it would be expected that the insoluble products from the green and brown oxychlorides would be identical, provided that products (1) and (2) as well as (5) and (6) were precipitated in equal proportions. The fact that these insoluble substances are clearly different in colour indicates a predominating replacement of the chlorine atom by either the carboxylic oxygen or the phenolic oxygen. To determine which was the more probable alternative, reactions were carried out with aqueous solutions of brown molybdenyl chloride and sodium phenoxide and sodium benzoate, respectively. In the case of the sodium phenoxide, molybdenum hydroxide was precipitated, whereas with the benzoate a well-characterised, insoluble derivative was obtained whose analysis corresponds to molybdenyl benzoate. These results indicate that in the case of reactions with sodium salicylate and compounds of tervalent molybdenum the carboxylic oxygen replaces the co-ordinated chlorine atom and that the reaction itself is dependent on the presence of the carboxyl group. Whether this conclusion be accepted or not, there is no doubt, from the nature of the colours of the products, that the chlorine atom is replaced almost exclusively by either the phenolic or the carboxylic oxygen, and so the proof of *cis-* and *trans-*isomerism reduces itself to demonstrating that one isomeride, the *trans-*, should yield one product by reaction with monosodium salicylate, and that the other isomeride, the *cis-*, should give rise to two products, neither identical with the foregoing. On the assumption that the carboxylic oxygen replaces the chlorine atom, the following scheme will obtain:



(a) *Trans-cis.*



(b) *Cis-cis.* (c) *Cis-trans.*

By reaction of the green molybdenyl chloride and monosodium salicylate, one insoluble green molybdenyl salicylate has been obtained, the configuration of which must be in accordance with (a). From the brown molybdenyl chloride there is evidence of one soluble isomeride (b) and one brick-red insoluble isomeride (c), which is actually distinct from (a), as anticipated on theoretical grounds. A *cis-*configuration has therefore been assigned to the brown oxychloride, and a *trans-* to the green oxychloride.

Reaction between Monosodium Salicylate and Brown Molybdenyl Chloride.—Equimolecular aqueous solutions of monosodium salicylate and molybdenyl chloride were mixed together. With highly concentrated solutions, a brick-red molybdenyl salicylate separated in a few minutes and an intensely red supernatant liquid was produced. From more dilute solutions, the solid was precipitated only after a longer period. In every case, however, the supernatant liquid was intensely red. On keeping, the red liquid continuously deposited the insoluble product, a process which was accelerated by warming. Undoubtedly two salicylates had been produced. One was insoluble in water whilst the other was readily soluble, producing a red solution. By intramolecular changes the soluble product was continuously changing to the insoluble isomeride.

Insoluble Molybdenyl Salicylate.—This solid was obtained as above, and, after filtration and washing free from the red, supernatant liquid by means of air-free water, it was dried in a desiccator over calcium chloride. The behaviour of the compound during the drying process is noteworthy. When the brick-red solid is dried out of contact with air, it darkens and ultimately yields the brown compound $[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O,2H_2O]H$. It is impossible to isolate the brick-red substance in a dry condition because of these changes, but it seems reasonable to assume that they are associated with a decreasing content of water. The brown solid is practically insoluble in water, but when freshly prepared it is soluble in alcohol and in acetone.

The acidic nature of the compound is indicated by its ready solubility in ammonia and in dilute solutions of sodium or potassium hydroxide. After a time, the solid loses its ability to dissolve in organic solvents and becomes less soluble in ammonia.

Analysis.—The molybdenum was determined both by ignition of the compound to molybdenum trioxide and by precipitation as sulphide and ignition to the trioxide. Combustion of the solid gave water derived from both the hydrogen and the water of constitution (Found: Mo, 33·45; C, 29·2; H_2O, 28·3.

$$[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O,2H_2O]H$$

requires Mo, 33·7; C, 29·5; $4{\cdot}5H_2O$ [from 9H], 28·4%). Analyses of other samples have indicated that the water content may vary between 2—$2{\cdot}5H_2O$.

Soluble Molybdenyl Salicylate.—Numerous attempts have been made to isolate a solid substance from the red, supernatant liquid formed in the interaction of the brown chloride and the sodium salicylate. Concentration of the liquid resulted in the formation of large quantities of the brown, insoluble isomeride, and the use of organic liquids neither precipitated nor extracted any product. The addition of pyridine, however, caused an immediate precipitation of a reddish-brown substance which, after washing and drying, proved to have the formula $\begin{matrix} C_5H_6N \\ MoO \end{matrix}\left[\begin{matrix} MoO\cdot O\cdot OC\cdot C_6H_4\cdot O \\ 3H_2O \end{matrix}\right]_2 H_2O$, which requires Mo, 35·4; C, 28·0; N, 1·7; $14H_2O$ (from 28H), 31·0 (Found: Mo, 35·2; C, 28·3; N, 1·6; H_2O, 30·0%).

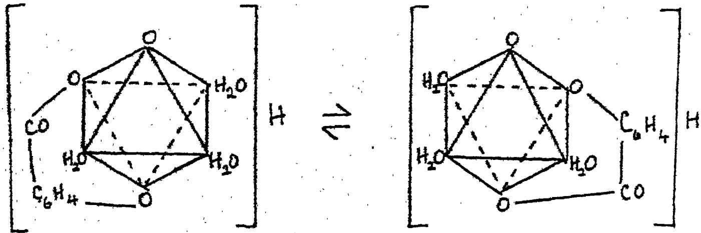
The isolation of this substance indicates the existence of the following equilibrium in the solution :

$$2[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O]H \rightleftharpoons MoO[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O] + OH\cdot C_6H_4\cdot CO_2H.$$

The addition of the pyridine disturbs the reaction in such a way as to form an increasing amount of $MoO[MoO\cdot O\cdot C_6H_4\cdot CO\cdot O]$, which is precipitated simultaneously with the pyridine salt of the soluble molybdenyl salicylate. Thus, although the molybdenyl salicylate has not been isolated, the results of the reaction with pyridine are strong evidence in favour of its existence and of its acidic character.

Reaction between Monosodium Salicylate and Green Molybdenyl Chloride.—On mixing an aqueous solution of sodium salicylate with a freshly-prepared, aqueous solution of green molybdenyl chloride, air being rigidly excluded, a pale green product was precipitated whilst the supernatant liquor was nearly colourless. The solid was separated and dried; a colour change from pale green to brown resulted, and the final product was almost identical in colour and properties with the dried insoluble molybdenyl salicylate prepared from the brown isomeric oxychloride. Analysis showed that the water content of the solid varied from 2—2·5H_2O (Found: Mo, 32·4; C, 28·2; H_2O, 29·55. $[O\cdot C_6H_4\cdot CO\cdot O\cdot MoO,2\cdot 5H_2O]H$ requires Mo, 32·65; C, 28·6; 5H_2O [from 10H], 30·6%).

A point of interest in connexion with the oxychlorides is that both the insoluble green molybdenyl salicylate and the insoluble brick-red isomeride give the same brown product on drying. Two explanations may be suggested. (1) This change of colour might be due to an intramolecular reaction whereby the same mixture of the isomerides (a) and (c) would result in both cases; there is the possibility that a brown product would result from a mixture of red and green substances. (2) An alternative view is that, by the loss of one molecule of water, the oxygen can occupy two positions in the co-ordination sphere—the analysis of the brown product indicates a water-content of 2—2·5H_2O—and it can readily be shown that by such a rearrangement the structures (c) and (a) become identical.



(c) *Cis-trans* (red). (a) *Trans-cis* (green).

This question of the co-ordination number of oxygen will be dealt with in a later communication.

The authors desire to thank Messrs. Brunner Mond and Co., Ltd., and the Chemical Society for grants in aid of this investigation. One of them (R. L. W.) gratefully acknowledges receipt of a grant from the Department of Scientific and Industrial Research for part of the time during which this work was in progress.

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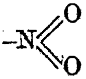
[*Received, October* 16*th*, 1926.]

XXIII.—*The Parachor and Chemical Constitution. Part IV. Three-membered and Four-membered Rings.*

By Samuel Sugden and Henry Wilkins.

(1) *Three-membered Rings.*

In the first paper on the parachor (Sugden, J., 1924, **125**, 1180), a provisional value of 22·3 was assigned to the constant for a three-membered ring. This was based upon a misconception of the structure of the nitro-group which has since been cleared up by the discovery of the effect of semipolar double bonds upon the molecular parachor (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525). From the data there discussed it appears probable that the nitro-group has the structure  $-\mathrm{N}{\begin{array}{l}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{array}}$ and does not contain a three-membered ring. In the present paper, data are given for nine substances which, from chemical evidence, undoubtedly possess a cyclic structure and from which the constant for a three-membered ring can be deduced.

The observed values of the parachors for these substances are in the second column of Table I; the column headed $\Sigma[P]$ gives the sum of the atomic and structural constants, except that for the three-membered ring, so that the effect of this structure is obtained by subtracting $\Sigma[P]$ from $[P]$ obs.

The mean value for the effect of the three-membered ring on the molecular parachor may be taken as 17, which is in good agreement with the figure predicted from the degree of unsaturation in such structures, as discussed later (Section 3). Individual substances give figures diverging by 3—4 units from this mean and such variations require consideration.

In the first place, these differences are much larger than the experimental errors of measurement. The estimated error in the density determinations is 0·1% and in the surface tensions 0·5%; if

TABLE I.

Parachor of Three-membered Rings.

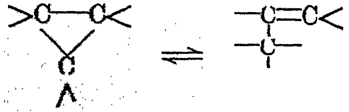
Substance.	[*P*] obs.	Σ[*P*].	Structural constant.	Error of measurement.
1. Ethylene oxide	112·5	98·0	14·5	0·2
2. Epichlorohydrin	193·7	174·2	19·5	0·4
3. Ethyl *cyclo*propane-1 : 1-dicarboxylate	417·1	402·6	14·5	0·8
4. Ethyl *cyclo*propane-1 : 2-dicarboxylate	422·8	„	20·2	0·8
5. Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate	701·1	688·2	12·9	1·4
6. Ethyl caronate	493·2	479·6	13·6	1·0
Esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid.				
7. *normal* Methyl ester	371·6	352·6	19·0	0·8
8. „ Ethyl „	450·2	430·6	19·5	0·9
9. *labile* „ „	447·8	430·6	17·2	0·9
		Mean	16·7	

both errors are in the same direction, then (since the fourth root of the surface tension is used) the parachor is uncertain to 0·2% at most. The possible error thus introduced in the determination of the constant for the three-membered ring is given in the last column of Table I; it will be seen that it is much smaller than the differences found in the structural constant.

Further, it does not seem possible to account for these differences by the presence of impurities in some of the substances examined. Nos. 5, 7, and 8 are solids at the ordinary temperature and were recrystallised to constant melting point, whilst Nos. 3 and 4 were esters prepared from recrystallised acids of sharp melting point and boiled within 1°. Of the remaining liquids, epichlorohydrin was available in considerable quantity and was repeatedly dried and fractionated without producing any change in the surface tension or density, and the values found for the latter are in good agreement with those given by previous observers. The figure for ethylene oxide is calculated from the observations of Maass and Boomer (*J. Amer. Chem. Soc.*, 1922, **44**, 1709) on a carefully purified specimen. The esters 4 and 9 were purified by fractional distillation only; they boiled within 1°, and the parachors found for them fall well within the limits of the variation of the constant for a three-membered ring, so that there is no reason to suppose that they are seriously in error.

Another possible explanation of these differences is that some of the substances examined exhibit tautomerism and are mixtures of

(I.)



(II.)

isomerides having the structures (I) and (II). If this were the case, the structural constant would approach that for a non-polar double bond (23·2) as the proportion of (II) increased. This explanation is excluded, however, for the substances having the structure (II) are in many cases well known and have different properties. Thus the esters 4, 5, and 6 are isomerides of, but not identical with, certain esters of the glutaconic series which have been well characterised.

It is obvious, therefore, that in this series, as in others (compare Sugden and Whittaker, J., 1925, **127**, 1868), the parachor is not strictly an additive function of atomic and structural constants, but that these constants vary slightly from substance to substance. The variation in the constant for the three-membered ring is in harmony with modern views as to the effect of substituents on the stability of rings; in particular, it is interesting to note that the lowest values, corresponding to a lower degree of unsaturation, are given by unsubstituted rings or by those containing a *gem*-group (compare Ingold, J., 1921, **119**, 305).

The figures for the esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid are of special interest in view of the peculiar type of isomerism exhibited by the derivatives of this acid (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342; 1925, **127**, 460). The parachors found for these substances show clearly that both the normal and labile esters contain a three-membered ring and a non-polar double bond; if the isomerism were due to the presence of a semipolar double bond in either the labile or the normal form, the parachor would have been 25 units lower. This explanation of the remarkable type of isomerism exhibited by these compounds would be compatible with the fact that both forms have been obtained optically active, but is definitely excluded by the data quoted in Table I.

(2) *Four-membered Rings.*

In a previous paper (Sugden, *loc. cit.*), the value 12·0 was allotted to the effect on the parachor on a four-membered ring; this figure was based on observations of the surface tensions of limonene and pinene by Mitchell and Smith (J., 1913, **103**, 489). We have now measured three derivatives of *cyclo*butane with the results shown in Table II. It will be seen that the new data give good confirmation

TABLE II.

	[*P*] obs.	Σ[*P*].	Four-membered ring.
Ethyl 1-cyano*cyclo*butane-1-carboxylate	360·4	348·8	11·6
Ethyl *cyclo*butane-1 : 1-dicarboxylate	454·1	441·6	12·5
Ethyl *cyclo*butanecarboxylate	309·4	298·8	10·6
		Mean	11·6

of the older value and are also in good agreement with the constant calculated from the degree of unsaturation (see Section 3).

These *cyclo*butane derivatives were prepared by the method of Perkin and Carpenter (J., 1899, 75, 921), and the esters measured were made *via* the silver salt from specimens of the free acids which had been carefully purified by crystallisation or distillation. The purification of the *cyclo*butane-1 : 1-dicarboxylic acid was effected by a specially devised method (see Experimental). The monocarboxylic ester prepared from this purified acid by the elimination of carbon dioxide and esterification boiled several degrees lower than Perkin and Carpenter's ester (*loc. cit.*), but its purity was confirmed by a determination of its saponification value.

(3) *Structural Constants and Unsaturation.*

It has been suggested in previous communications that the principal factor which determines the value of structural parachors is the intensity of unsaturation. This idea can now be expressed quantitatively, as all the more important constants are known with a fair degree of accuracy.

In Table III, col. 2 gives the number of latent valencies in the structure indicated in col. 1, or the number of hydrogen atoms required to convert each structure into an open-chain saturated compound. Col. 3 gives the number of octets which share this unsaturation, whilst col. 4 gives the ratio x/n, which may be termed the degree of unsaturation. If it is assumed that the structural parachor is proportional to the degree of unsaturation, then, from the experimental value for the double bond (which is based upon the largest number of observations), the parachors for the other structures can be calculated. The numbers thus obtained are in col. 6, and they are seen to be in good agreement with the experimentally determined values in col. 5.

TABLE III.

Structure.	Latent valencies (x).	Octets (n).	Degree of unsaturation (x/n).	Parachor.	
				Obs.	Calc.
Triple bond	4	2	2·000	46·6	46·4
Double bond	2	2	1·000	(23·2)	(23·2)
Three-membered ring	2	3	0·667	17	15·5
Four-membered ring	2	4	0·500	11·6	11·6
Five-membered ring	2	5	0·400	8·5	9·3
Six-membered ring	2	6	0·333	6·1	7·7

EXPERIMENTAL.

In the course of this work new measurements have been made of the surface tension and density of eleven compounds. The surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); the constants for the bubbles used are:

Apparatus	4c.	4d.	5a.	8a.	9a.
r_2 (cm.)	0·139	0·139	0·140	0·206	0·216
A	0·004790	0·007767	0·006805	0·003712	0·00536

Densities were determined by the **U**-shaped pyknometer previously described (J., 1924, **125**, 1171) and are given in g./c.c. All temperatures recorded were obtained by comparison with a standard thermometer with *N.P.L.* certificate and are corrected for exposed stem.

The tables below are set out in the same manner as in previous papers and do not need further description. The parachor in the last column is calculated by the formula $[P] = \gamma^{1/4}M/(D - d)$, where γ is the surface tension, M the molecular weight, D the density of the liquid, and d the density of the vapour.

Ethylene oxide, C_2H_4O; $M = 44{\cdot}04$. The values of γ, D, and d are taken from the paper of Maass and Boomer (*loc. cit.*).

t.	γ(dynes/cm.).	$(D-d)$ (g./c.c.).	Parachor.
−52·0°	36·4	0·9657	112·0
−43·4	34·8	0·9545	112·1
−26·2	31·9	0·9316	112·4
−15·0	30·3	0·9164	112·7
− 5·0	28·4	0·9027	112·6
5·8	26·8	0·8879	112·9
13·3	25·4	0·8805	112·3
20·0	24·3	0·8679	112·7
		Mean	112·5

Epichlorohydrin, C_3H_5OCl, $M = 92{\cdot}51$, was dried over calcium chloride and boiled at 115° (corr.)/740 mm. Densities determined: $D^{10°}_{4°}$ 1·190, $D^{33°}_{4°}$ 1·161, $D^{55°}_{4°}$ 1·136, $D^{71°}_{4°}$ 1·116, whence $D^{t°}_{4°} = 1{\cdot}202 - 0{\cdot}00119t$. These values are in good agreement with those of Thorpe (J., 1880, **37**, 207).

App.	t.	P.	D.	ϕ.*	γ.	Parachor.
9a	12·5	6939	1·187	1·0250	38·13	193·6
,,	31	6447	1·165	1·0264	35·48	193·7
,,	50·5	5964	1·142	1·0280	32·86	193·9
,,	68·5	5504	1·121	1·0298	30·38	193·7
,,	89	5011	1·096	1·0320	27·72	193·6
					Mean	193·7

* A correction factor, see J., 1924, **125**, 31.

Ethyl cyclo*propane*-1 : 1-*dicarboxylate*, $C_9H_{14}O_4$, $M = 186{\cdot}2$, was prepared *via* the silver salt from purified acid which had been recrystallised from benzene until its melting point was constant. The ester boiled at 218° (corr.)/769 mm. Densities determined:

$D_{4°}^{15°}$ 1·071, $D_{4°}^{50°}$ 1·034, $D_{4°}^{93°}$ 0·988, $D_{4°}^{139°}$ 0·940, whence $D_{4°}^{t°} = 1·087 - 0·00105t$.

App.	t.	P.	D−d.	φ.	γ.	Parachor.
4c	25	6430	1·061	1·0155	31·28	415·1
9a	75	4712	1·008	1·0313	26·05	417·4
4c	110	4633	0·971	1·0197	22·62	418·3
9a	134	3641	0·946	1·0380	20·25	417·6
4c	153	3780	0·925	1·0230	18·52	417·7
9a	164	3141	0·914	1·0425	17·55	417·1
4c	189	3156	0·887	1·0264	15·52	416·7
					Mean	417·1

Ethyl cyclo*propane*-1 : 2-*dicarboxylate*, $C_9H_{14}O_4$, *M* = 186·2, was twice distilled under diminished pressure; the specimen used boiled at 106·5—107·5° (corr.)/11 mm. Densities determined: $D_{4°}^{13°}$ 1·062, $D_{4°}^{54°}$ 1·020, $D_{4°}^{81°}$ 0·993, whence $D_{4°}^{t°} = 1·075 - 0·00101t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
5a	11	4810	1·064	1·0210	33·41	420·9
8a	14	8802	1·061	1·0168	33·22	421·3
5a	54	4154	1·020	1·0233	28·92	423·4
8a	71	7215	1·003	1·0194	27·29	424·3
5a	90	3607	0·984	1·0258	25·17	423·9
					Mean	422·8

Ethyl cyclo*propane*-1 : 1 : 2 : 2-*tetracarboxylate*, $C_{15}H_{22}O_8$, *M* = 330·2, was recrystallised from ligroin and melted sharply at 43° (corr.). Densities determined: $D_{4°}^{57°}$ 1·117, $D_{4°}^{69°}$ 1·104, $D_{4°}^{77°}$ 1·096, $D_{4°}^{83·2°}$ 1·090, whence $D_{4°}^{t°} = 1·176 - 0·00104t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
5a	76	4170	1·097	1·0250	29·08	699·0
,,	97	3876	1·075	1·0264	27·08	700·8
,,	122	3537	1·049	1·0282	24·75	702·2
,,	152	3127	1·018	1·0308	21·93	702·2
					Mean	701·1

Ethyl caronate (*ethyl* trans-3 : 3-*dimethyl*cyclo*propane*-1 : 2-*dicarboxylate*), $C_{11}H_{18}O_4$, *M* = 214·2, was prepared from recrystallised caronic acid and absolute alcohol and boiled at 244° (corr.)/762 mm. Densities determined: $D_{4°}^{11°}$ 1·035, $D_{4°}^{30·5°}$ 1·015, $D_{4°}^{53°}$ 0·992, $D_{4°}^{71°}$ 0·973, whence $D_{4°}^{t°} = 1·046 - 0·00103t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
4d	12	3965	1·034	1·0245	31·56	491·0
,,	34	3662	1·011	1·0260	29·19	492·5
,,	54	3395	0·990	1·0275	27·10	493·7
,,	63·5	3258	0·981	1·0283	26·02	493·1
,,	75	3128	0·969	1·0291	25·00	494·3
,,	93·5	2890	0·950	1·0309	23·15	494·6
					Mean	493·2

normal *Methyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_8H_{10}O_4$, *M* = 170·1. White crystals, m. p. 33—34° (corr.). Densities determined: $D_{4°}^{39°}$ 1·123, $D_{4°}^{57°}$ 1·103, $D_{4°}^{71°}$ 1·087, $D_{4°}^{91°}$ 1·064, whence $D_{4°}^{t°} = 1·169 - 0·00115t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
4d	42	4460	1·121	1·0237	35·46	370·3
,,	63	4138	1·097	1·0250	32·94	371·4
,,	81	3863	1·076	1·0262	30·79	372·4
,,	95	3632	1·060	1·0275	28·98	372·3
					Mean	371·6

normal *Ethyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_{10}H_{14}O_4$, $M = 198·1$. White crystals, m. p. 38—39° (corr.). Densities determined: $D_{4°}^{44·5°}$ 1·038, $D_{4°}^{60·5°}$ 1·024, $D_{4°}^{81·5°}$ 1·001, whence $D_{4°}^{t°} = 1·084 - 0·00100t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
4d	41·5	3947	1·042	1·0248	31·42	450·1
,,	51	3803	1·033	1·0255	30·33	450·1
,,	62	3653	1·022	1·0263	29·12	450·2
,,	77·5	3448	1·007	1·0275	27·52	450·6
					Mean	450·2

labile *Ethyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_{10}H_{14}O_4$, $M = 198·1$. This ester was prepared by distilling the normal ester at atmospheric pressure (compare Goss, Ingold, and Thorpe, *loc. cit.*). Considerable decomposition and gas evolution took place; the distillate fractionated under diminished pressure gave a 50% yield of an oil, b. p. 155—156° (corr.)/19 mm., which was regarded as the labile ester. Densities determined: $D_{4°}^{23°}$ 1·072, $D_{4°}^{40·5°}$ 1·054, $D_{4°}^{64·5°}$ 1·029, whence $D_{4°}^{t°} = 1·096 - 0·00103t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
4d	26	4275	1·069	1·0235	33·98	447·5
,,	50	3911	1·045	1·0252	31·13	447·8
,,	77	3507	1·017	1·0273	27·99	448·0
					Mean	447·8

Ethyl 1-*cyano*cyclo*butane*-1-*carboxylate*, $C_8H_{11}O_2N$, $M = 153·1$. The crude ester was prepared by the condensation of cyanoacetic ester and trimethylene bromide (Perkin and Carpenter, *loc. cit.*); the yield was low in the first runs, but was raised to 67% by using alcohol dried with the aluminium–mercury couple. The crude ester (b. p. 99—102°/14 mm.) was partly hydrolysed with a slight excess of methyl-alcoholic potash, and the free cyano-acid recrystallised twice from benzene; it then melted sharply at 67—68° (corr.). From this, the ethyl ester was prepared *via* the silver salt and boiled at 215·5—216° (corr.)/762 mm. Densities determined: $D_{4°}^{13·5°}$ 1·045, $D_{4°}^{43°}$ 1·015, $D_{4°}^{70·5°}$ 0·988, $D_{4°}^{93°}$ 0·966, whence $D_{4°}^{t°} = 1·058 - 0·000995t$.

App.	t.	P.	D.	φ.	γ.	Parachor.
4d	13·5	4495	1·045	1·0219	35·68	358·1
,,	46	4011	1·012	1·0237	31·88	359·5
,,	57	3887	1·001	1·0242	30·92	360·7
,,	69·5	3673	0·989	1·0253	29·26	360·1
,,	84·5	3495	0·974	1·0262	27·86	361·1
,,	111·5	3128	0·947	1·0285	24·99	361·5
,,	126·5	2936	0·932	1·0299	23·49	361·7
					Mean	360·4

Ethyl cyclo*butane*-1 : 1-*dicarboxylate*, $C_{10}H_{16}O_4$, $M = 200\cdot2$. The crude cyano-ester on complete hydrolysis gave a mixture of the required dibasic acid and malonic acid derived from unchanged cyanoacetic ester. This mixture was difficult to separate by crystallisation from any solvent, but the malonic acid was removed completely in the following manner. The mixed acids were dissolved in excess of 5% ammonia, and barium chloride solution was added until no further precipitate was produced. The precipitate of barium malonate was filtered off, and the filtrate, after acidification and extraction with ether, gave nearly pure *cyclo*butane-1 : 1-dicarboxylic acid, which, after one crystallisation from benzene, melted at 156·5° (corr.). From this, the ester was prepared *via* the silver salt; b. p. 228·5—229·5° (corr.)/755 mm. Densities determined: $D_{4^\circ}^{15\cdot5^\circ}$ 1·054, $D_{4^\circ}^{51\cdot5^\circ}$ 1·017, $D_{4^\circ}^{79^\circ}$ 0·990, $D_{4^\circ}^{99^\circ}$ 0·969, whence $D_{4^\circ}^{t^\circ} = 1\cdot070 - 0\cdot00102t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	15	4086	1·054	1·0243	32·51	453·5
,,	49	3601	1·0195	1·0266	28·70	454·4
,,	81	3157	0·987	1·0294	25·24	454·5
					Mean	454·1

Ethyl cyclo*butanecarboxylate*, $C_7H_{12}O_2$, $M = 128\cdot1$. The pure dicarboxylic acid lost carbon dioxide smoothly at 185—190° and gave a good yield of the monobasic acid, b. p. 190—192° (corr.)/762 mm. The ethyl ester prepared *via* the silver salt was repeatedly fractionated and boiled at 152—154° (corr.)/756 mm. (Perkin and Carpenter give 159—162°). The purity of the ester was therefore checked by a determination of its equivalent by hydrolysis with potash (Found: 127·0. Calc.: 128·1). Densities determined: $D_{4^\circ}^{31^\circ}$ 0·956, $D_{4^\circ}^{45\cdot5^\circ}$ 0·941, $D_{4^\circ}^{60^\circ}$ 0·927, $D_{4^\circ}^{74\cdot5^\circ}$ 0·911, whence $D_{4^\circ}^{t^\circ} = 0\cdot988 - 0\cdot00103t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	19·5	3766	0·968	1·0242	29·96	309·5
,,	47·5	3335	0·939	1·0265	26·58	309·6
,,	70	3016	0·916	1·0286	24·10	309·8
,,	90·5	2707	0·895	1·0311	21·68	308·8
					Mean	309·4

Summary.

1. The "structural" parachor for a three-membered ring is found to be 17; individual substances show variations of a few units from this value.

2. Both the normal and the labile forms of esters of 3-methyl*cyclo*propenedicarboxylic acid contain a non-polar double bond.

3. The value for a four-membered ring is shown to be 11·6.

4. Structural parachors are proportional to the degree of unsaturation of the multiple bond or ring structure concerned.

The authors wish to express their thanks to Prof. C. K. Ingold, F.R.S., for the loan of substances 4, 5, 7, and 8 in Table I, and to Mr. R. G. Atkinson for a specimen of synthetic caronic acid. One of us (S. S.) is also indebted to the Research Fund Committee of this Society for a grant which has partly defrayed the cost of this investigation.

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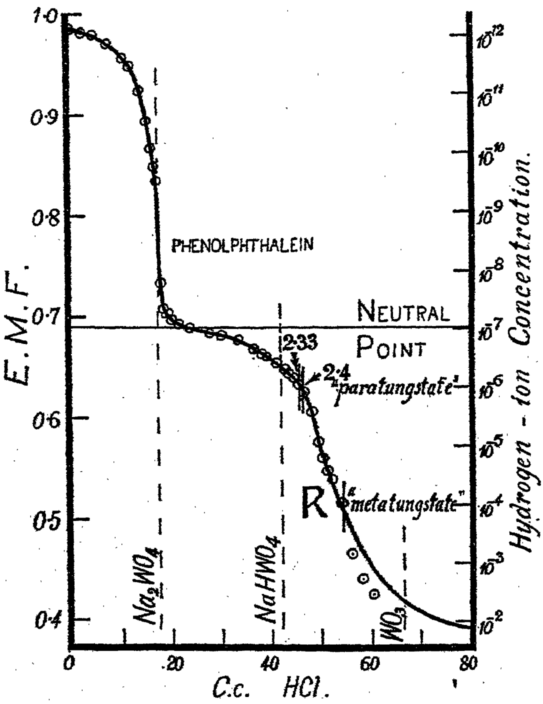
XXIV.—*An Electrometric Study of Tungstic Acid.*

By HUBERT THOMAS STANLEY BRITTON.

THE facts that tungstic oxide forms salts with the alkali metals, R_2WO_4, and that tungsten appears in the same group of the periodic system as sulphur have led to the impression that tungstic acid is an ordinary dibasic acid. An attempt was made to study the acidic nature of the oxide by following electrometrically the variation in hydrogen-ion concentration during the course of its neutralisation with sodium hydroxide; for this purpose, however, it was found more convenient to back-titrate a solution of the oxide in sodium hydroxide with hydrochloric acid. The first portion of the titration curve, given in Fig. 1, was constructed from *E.M.F.* measurements at 20° made between a hydrogen electrode immersed in the solution and a normal calomel half-element, the junction liquid being a saturated solution of potassium chloride. The titration was performed as previously described (J., 1924, **125**, 1572) and the *P.D.*'s were found to be reproducible until 0·5 volt was reached ($[H^{\cdot}] = 10^{-4}$). At this stage, the hydrogen in the electrode began to reduce catalytically the sexavalent tungsten to the quinquevalent state, as indicated by the appearance of the characteristic blue coloration around the electrode. This position is denoted by R on the curve. The three points on the diagram obtained after reduction became obvious represent initial readings made before the effect of the reduction had become appreciable. To complete the titration curve, resort was made to the oxygen electrode, with which a similar titration was carried out using solutions of the same concentrations. Neither the hydrogen-electrode nor the oxygen-electrode curve showed that any abrupt changes in hydrogen-ion concentration occurred in solutions more acidic than p_H 4. The remaining portion of the curve in Fig. 1 was plotted from the oxygen-electrode curve, calibrated against the portion obtained with the hydrogen electrode, the accuracy of which is considered to be of the order of one-tenth of a p_H unit (compare J., 1924, **125**, 1572; 1925, **127**, 1896). The curve given in Fig. 1 represents the titration by 0·1020*N*-hydrochloric acid of 100 c.c. of a solution which was 0·0678*N* with respect to sodium hydroxide and 0·0250*M* with respect to tungstic acid (WO_3).

The curve shows that a sharp diminution in p_H took place with the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate.

FIG. 1.



This explains why tungstic acid may be estimated volumetrically either by titrating a suspension of it directly with sodium hydroxide or by dissolving the oxide in alkali and titrating the excess of alkali with acid, using in each case phenolphthalein as indicator (Hundeshagen, *Chem.-Ztg.*, 1894, **18**, 547; Herting, *Z. angew. Chem.*, 1901, **14**, 165; Lind and Trueblood, *J. Amer. Chem. Soc.*, 1907, **29**, 477). The remaining part of the curve down to the dotted line indicating WO_3 represents, in effect, the reverse of the neutralisation of tungstic acid with sodium hydroxide. The large inflexion produced when the acid was about one-quarter neutralised is surprising in that it did not occur when the acid was half neutralised, as would have been the case had tungstic acid behaved as an ordinary dibasic acid with widely differing dissociation constants.

No precipitation of tungstic oxide occurred throughout the titration even although a large excess of hydrochloric acid had been added. The solution remained perfectly clear, suggesting that the oxide had passed into a sub-colloidal state and not into combination with the hydrochloric acid, which would have been indicated by the p_H readings. It is of course possible that the hydrochloric acid had some stabilising influence through being slightly adsorbed by or feebly combined with the tungstic oxide. Using more concentrated solutions, precipitation ensues (see van Liempt, *Z. anorg. Chem.*, 1923, **127**, 215; *Rec. trav. chim.*, 1924, **43**, 30).

The curve throws some light on the so-called "paratungstates" and "metatungstates." Sodium paratungstate is stated to have the composition $3Na_2O,7WO_3,21H_2O$ or $5Na_2O,12WO_3,28H_2O$, and thus it contains either 2·33 or 2·4 mols. of Na_2O to 1 mol. of WO_3. The points on the titration curve marked 2·33 and 2·4 indicate the hydrogen-ion concentrations of the solutions when the solutes were present in those ratios, the p_H being 6·1 and 6·0, respectively. Schmidt (*Amer. Chem. J.*, 1886, **8**, 16) found that a solution of the 2·4-salt was acidic to rosolic acid and alkaline to cochineal; consequently the p_H of his solution was in the neighbourhood of 6, and is thus in accord with the value indicated by the curve. The point marked "metatungstate" gives the hydrogen-ion concentration, 10^{-4}, of the solution when the alkali in combination with the tungstic acid was that required by $Na_2W_4O_{13}$, the formula for sodium metatungstate. Although the hydrogen-ion concentrations of the "para" and "meta" solutions show that some kind of union has taken place, it is difficult to picture the exact nature of that union. It appears from the curve that the paratungstate solution is the same as that of a solution of sodium tungstate saturated with tungstic oxide such that the change in hydrogen-ion concentration undergone is very small, whereas the metatungstate solution corresponds to a still greater saturation, but one which involves a considerable variation in hydrogen-ion concentration. These are the conditions which underlie the preparation of these salts. Seeing that tungstic acid cannot be considered as an ordinary dibasic acid, it is not apparent what kind of compounds these are, unless it be supposed that they contain tungstic acid either in a polymerised form or in a semi-colloidal form, which on dissolution in water gives rise to a micellar ionisation.

The author thanks the Department of Scientific and Industrial Research for a personal grant, the Chemical Society for a Research Grant, and Prof. Philip, F.R.S., for kindly placing facilities at his disposal.

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LONDON, S.W. 7. [*Received, December 1st*, 1926.]

XXV.—*Complex Formation amongst the Nitrates. Part I. The Ternary System Copper Nitrate–Cobalt Nitrate–Water.*

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NITRATO-SALTS or double nitrates have not been investigated with thoroughness. The known examples are generally confined to cases where one metal is of high atomic weight and volume, *e.g.*, $3Ni(NO_3)_2,2Ce(NO_3)_3,24H_2O$ and $2KNO_3,Ba(NO_3)_2$, although some nitrato-acids are also known. It was noticed that a mixture of copper and cobalt nitrates set to a hard mass on keeping. This phenomenon has generally been held to indicate chemical or physical reaction, whilst Hedvall and Heuberger (*Z. anorg. Chem.*, 1924, **135**, 49) and Tammann (*ibid.*, 1925, **149**, 21) have measured the rate of reaction in powdered mixtures of crystals.

The Binary Systems.

(i) *Copper Nitrate–Water.*—The hydrates of copper nitrate have been extensively studied; the anhydrous nitrate has been prepared by Ditte (*Compt. rend.*, 1879, **89**, 576, 641) and by Guntz and Martin (*Bull. Soc. chim.*, 1909, **5**, 1004). Certain complexes are known containing anhydrous copper nitrate. Funk (*Z. anorg. Chem.*, 1899, **20**, 412), from a solubility curve, inferred the existence of a nona-, a hexa-, and a tri-hydrate, and these have been generally accepted although Richards (*Amer. Chem. J.*, 1898, **20**, 706, footnote) suggested that the formula of the so-called trihydrate should be $3Cu(NO_3)_2,8H_2O$. Schreinemakers, Berkhoff, and Posthumus (*Rec. trav. chim.*, 1924, **43**, 508) showed that the hydrate crystallising from ternary mixtures of copper nitrate, ammonium nitrate, and water has the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$. This is fully confirmed in the present work and in unpublished analyses by one of the authors of the ternary system copper nitrate–silver nitrate–water; in the first case the tie-lines intersect the copper nitrate–water side of the triangle at points corresponding to 80·9, 80·8, and 80·2% $Cu(NO_3)_2$ [Calc. for $Cu(NO_3)_2,2\frac{1}{2}H_2O$: 80·6; for

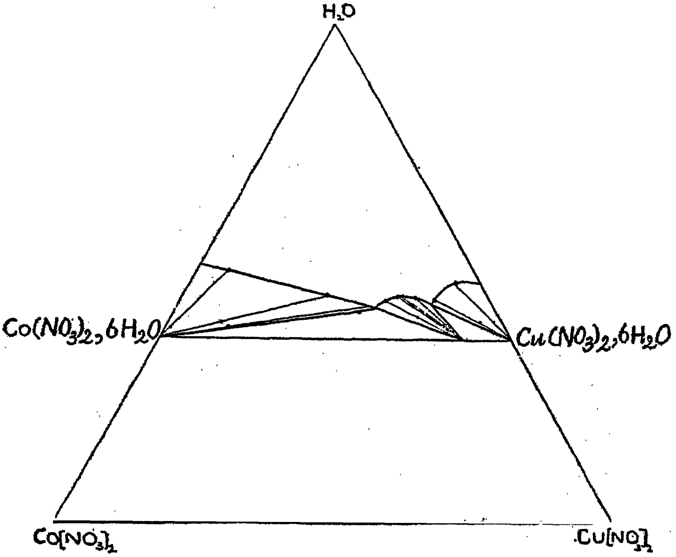
$3Cu(NO_3)_2,8H_2O$: 79·6%]. The crystals which Richards analysed were isolated from the binary system and kept over strong caustic potash solution : it is possible that they contained mother-liquor.

The solubility of copper nitrate in water at various temperatures is given in Table I as g. of $Cu(NO_3)_2$ per 100 g. of solution.

TABLE I.

Temp.	$Cu(NO_3)_2$ (%).	Hydrate present.	Temp.	$Cu(NO_3)_2$ (%).	Hydrate present.
15·0°	52·8	$6H_2O$.	30·0°	61·4	$2\frac{1}{2}H_2O$.
20·0	55·6	,,	35·0	62·0	,,
25·0	60·1	,,	40·0	62·6	,,
25·4	60·8	$6H_2O,2\frac{1}{2}H_2O$.			

FIG. 1.



Temp. 14°.

These results differ from those of Funk (*loc. cit.*), especially at the higher and lower temperatures. In addition, the temperature of the transition point is 25·4°, whereas Funk gives 24·5°—this is probably a misprint, as this point lies off his curve. Meijer (*Rec. trav. chim.*, 1924, **43**, 397), in examining the system copper nitrate–ammonium nitrate–water, obtained certain values for the solubility of copper nitrate in water, but as he failed to isolate the compound described by Schreinemakers, Berkhoff, and Posthumus (*loc. cit.*) from the same system, and as he did not question the existence of the trihydrate, it is not surprising that his solubility values depart largely from the above.

(ii) *Cobalt Nitrate–Water.*—Within the temperature limits of this investigation, this system does not call for detailed criticism: the solubilities as given by Funk (*Z. anorg. Chem.*, 1899, **20**, 412) seem to be consistently too high: the values now obtained are given in Table II, the solid phase throughout being $Co(NO_3)_2,6H_2O$.

TABLE II.

Temp.	15·0°	20·0°	25·0°	30·0°
$Co(NO_3)_2$ (%)	47·7	49·3	50·7	52·8

The Ternary System.

Three temperatures were chosen for investigation: 30°, just above the copper nitrate transition point; 20°, just below it; and 14°, at which a double salt was found to exist (see Fig. 1). This compound has the probable formula $6Cu(NO_3)_2,Co(NO_3)_2,42H_2O$,

TABLE III.

Temperature 14°.

	Solution.		Residue.		
$d^{20°}_{20°}$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	Solid phase.
—	52·5	—	—	—	$Cu(NO_3)_2,6H_2O$.
—	47·0	5·9	60·2	1·5	,,
—	45·6	11·1	58·8	3·0	,,
—	41·5	14·0	52·8	9·4	Double salt.
—	38·9	16·0	50·2	10·8	,,
—	38·4	16·7	51·3	10·4	,,
—	36·5	19·0	47·4	12·6	,,
—	34·1	22·8	9·6	51·9	$Co(NO_3)_2,6H_2O$.
—	25·8	28·7	7·9	52·8	,,
—	5·2	44·3	1·5	59·0	,,
—	—	47·5	—	—	,,

Temperature 20°.

$d^{20°}_{20°}$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	Solid phase.
—	55·6	—	—	—	$Cu(NO_3)_2,6H_2O$.
1·707	49·8	8·9	58·9	3·1	,,
—	49·4	10·8	57·8	4·9	,,
—	45·0	16·7	20·0	42·5	$Co(NO_3)_2,6H_2O$.
1·773	43·1	17·9	19·4	43·2	,,
1·705	33·7	24·5	14·8	46·7	,,
1·640	20·3	34·2	7·2	52·9	,,
1·613	13·1	38·9	3·4	56·8	,,
1·610	9·9	41·2	3·0	57·0	,,
1·598	—	49·3	—	—	,,

Temperature 30°.

$d^{20°}_{20°}$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	% $Cu(NO_3)_2$.	% $Co(NO_3)_2$.	Solid phase.
—	61·4	—	—	—	$Cu(NO_3)_2,2\frac{1}{2}H_2O$.
—	54·9	5·3	68·7	2·5	,,
—	48·4	13·0	75·9	1·9	,,
—	45·7	16·5	71·2	4·1	,,
—	37·9	22·2	9·8	52·4	$Co(NO_3)_2,6H_2O$.
—	27·1	29·2	5·6	55·5	,,
—	9·2	44·7	2·2	59·4	,,
—	—	52·7	—	—	,,

is very deliquescent, and melts at *ca.* 17°; as it is decomposed by water, its composition cannot be determined very accurately, the uncertainty corresponding to about $1H_2O$. The double salt is smoke-blue and crystallises from a magnificent purple solution.

The solutions and corresponding residues were examined in each case, and the data are in Table III.

Cobalt was determined by conversion of both metals to sulphate and electrolysis of the ammoniacal formate solution after removal of copper. Copper was determined by electrolysis of the nitric acid solution and also iodometrically: concordant results were obtained. A further check was made in the binary systems by determining both cobalt and copper as the anhydrous sulphates.

Summary.

1. The ternary system copper nitrate–cobalt nitrate–water has been examined at 14°, 20°, and 30°.

2. A complex has been isolated containing 6 mols. of the hexahydrate of copper nitrate to 1 mol. of the hexahydrate of cobalt nitrate, *i.e.*, $6Cu(NO_3)_2,Co(NO_3)_2,42H_2O$.

3. Copper nitrate "trihydrate" is shown to have the composition $Cu(NO_3)_2,2\frac{1}{2}H_2O$.

The authors tender their thanks to the Research Fund Committee of the Chemical Society for a grant which has covered the cost of the materials used.

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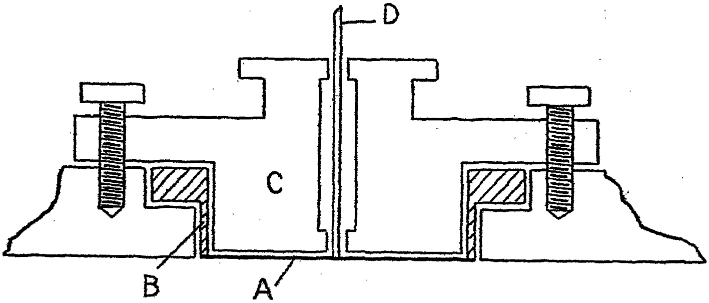
XXVI.—*The Movement of Flame in Closed Vessels: Correlation with Development of Pressure.*

By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER.

IT has been generally assumed in the past that, when a highly explosive mixture is ignited at the centre of a sphere, the moment of attainment of maximum pressure must synchronise with the moment of complete inflammation of the mixture, *i.e.*, with the moment at which the flame, the propagation of which follows regular concentric spherical surfaces, reaches the boundary of the vessel, which it does simultaneously at all points (see J., 1925, **127**, 764).

Langen ("Mitteilungen u. Forschungsarbeiten aus dem Gebeite des Ingenieurwesens," 1903, 8) seems to have been the first to realise that, if this assumption be correct, the interpretation of time–pressure diagrams, and particularly of cooling-curves, obtained by means of a continuously recording pressure-gauge attached to the wall of the explosion-vessel, can best be made when the vessel is spherical and ignition central. His experiments, made mainly for the purpose of determining the specific heats of gases at high temperatures, were therefore carried out under such conditions, his explosion-vessel having a spherical cavity of 33·5 litres capacity. Regarding such work, Dugald Clerk ("The Gas, Petrol, and Oil Engine," Vol. 1, p. 136, London, 1910) stated that "all physicists who have experimented on the subject agree in considering that inflammation is complete * when the highest pressure is attained."

FIG. 1.



This assumption has recently been challenged. Wheeler (J., 1918, **113**, 840) obtained experimental proof of the fact that in mixtures of methane and air containing between 7·5 and 12·5% of methane, ignited at the centre of a spherical bomb of 4 litres capacity, the times taken for the attainment of maximum pressure (measured from the moment of ignition) synchronised with the times taken for the flame to reach the walls; but the measurements of the last-named time-intervals were made by means of a "screen-wire" method which might have involved an indeterminate experimental error. It seemed desirable, therefore, to attempt direct synchronisation of the rate of development of pressure and the rate of spread of flame in an explosive mixture by simultaneous photographic registration on a rapidly revolving drum.

The apparatus devised for our purpose consists of an explosion-vessel (Plate I) of phosphor-bronze, the interior of which can be rendered spherical or cubical at will, fitted with windows through which the flame can be photographed and with a pressure-gauge of the diaphragm type.

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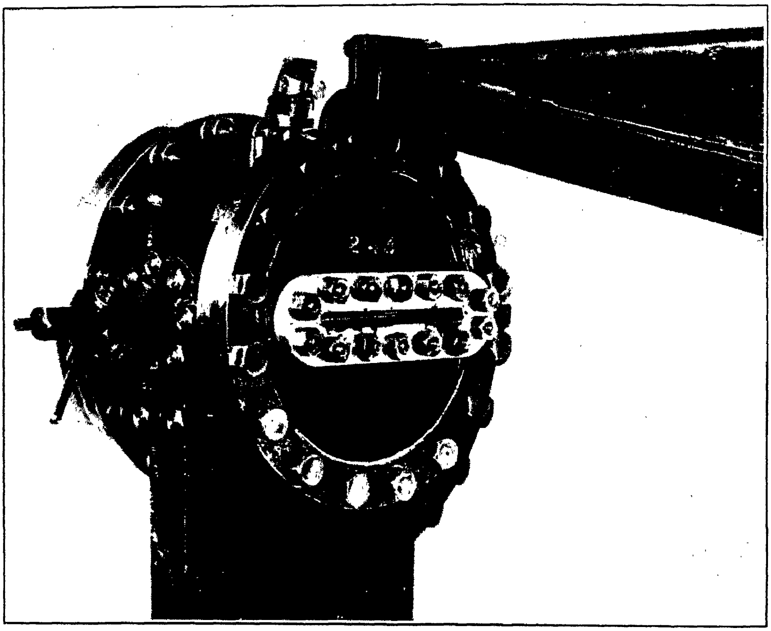
* Meaning, thereby, the complete spread of flame throughout the vessel, but not necessarily complete combustion.

PLATE I.



[*To face p.* 154.]

PLATE II.

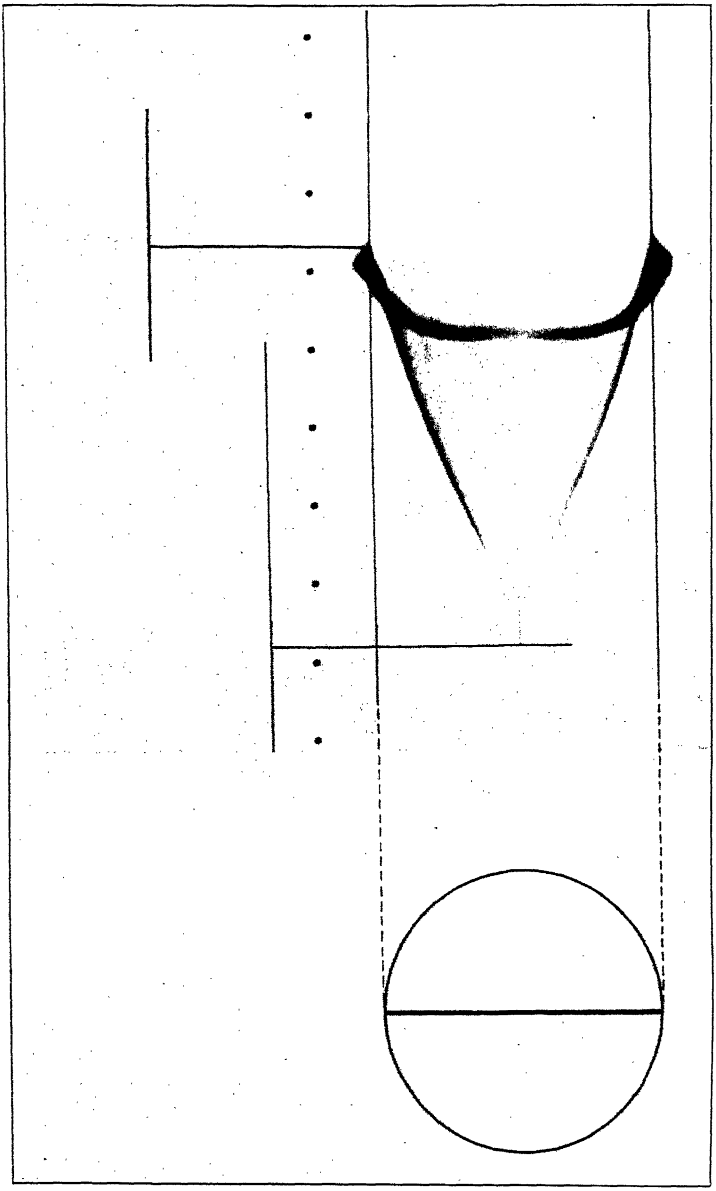
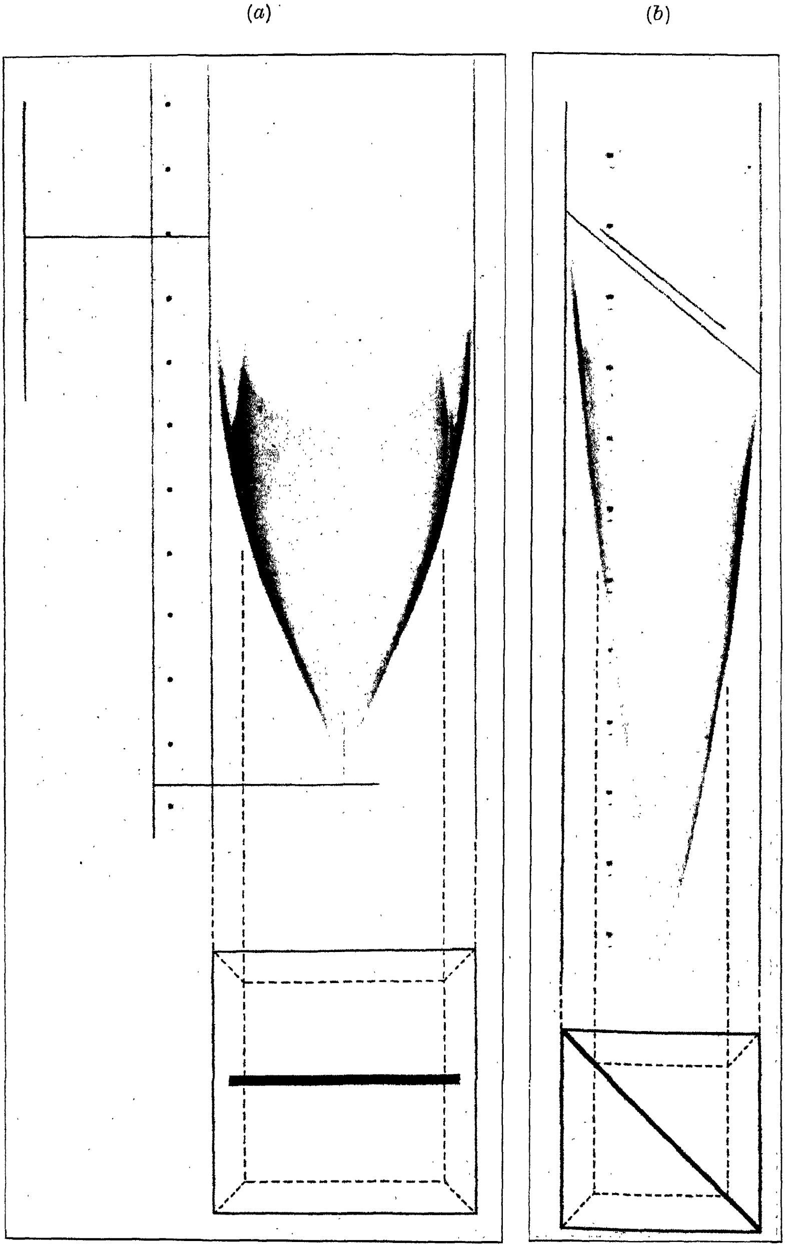


PLATE III.



(*a*) Window horizontal. (*b*) Window diagonal.

The pressure-gauge (Fig. 1), which is a modification of that designed by Rice (*U. S. Bureau of Mines, Bull. No.* 167, p. 51, 1922), has an optical indicator which is so arranged as to throw a spot of light on the same revolving drum as is used for obtaining a photographic record of the movement of the flame. The diaphragm, A, is of steel, 0·051 mm. thick, gold-plated to resist corrosion, and fitted flush with the inner surface of the explosion-vessel. It forms the base of a cylinder, B, of 34·92 mm. diameter, machined from tool-steel and having a thick collar to avoid distortion when clamped firmly in position by the flanged plug, C. Through a hole in this plug passes a rod, D, 1·59 mm. in diameter, one end of which is in contact with the diaphragm, the other being attached to a bell-and-crank lever which bears against a lever carrying a small mirror.

For the experiments described in this paper, the explosive mixtures were of carbon monoxide and air, saturated with water vapour at 19°. Ignition was effected exactly at the centre of the vessel by means of a secondary discharge at a 1·5 mm. spark-gap between platinum electrodes sheathed side by side within a glass rod of 3 mm. diameter. This rod fitted into a recess in an insulating plug of bakelite in the wall of the vessel, suitable electrical connexions to the electrodes being made through it to terminals outside.

Explosions within a Sphere.—The spherical cavity of the explosion-vessel was 14·8 cm. in diameter. In order to obtain a photograph of the flame within it, a slit, 2 mm. wide, was cut half-way through the walls horizontally from the window. There were thus left two thin, fin-shaped slots in the sides of the casting abutting on the window, in which, as appears in the photographs, flame was forced during the explosions. When the camera lens was focussed on the spark-gap, there was obtained during an explosion a record on the revolving drum of the movement of the flame in a horizontal plane in both directions from the spark. Such a photograph of the flame in a 60% carbon monoxide–air mixture is reproduced (reduced in size) on Plate II. The boundary of the spherical cavity is indicated on this photograph by the parallel lines drawn thereon as projections from the slit shown diagrammatically at the bottom. The flame forced (towards the camera and therefore out of focus) into the fin-shaped slots previously mentioned, appears as a collar around the upper part of the record. It will be noticed, also, that the image of the flame is divided equally into portions of different densities. This is due to the flame being partly obscured by the glass rod covering the electrodes.

The record also bears the time–pressure chart. It will be seen that the moment of attainment of maximum pressure corresponds almost exactly with the moment at which the flame reached the sides of the vessel.

Measurements made from this and similar records obtained with other mixtures of carbon monoxide and air are summarised in Table I.

TABLE I.

Explosions of Carbon Monoxide and Air within a Sphere. (*Mixtures Saturated with Water-vapour at* 19°.)

	Time-intervals (in 1/100ths of a second).		
CO (%).	(1) Between ignition and attainment of maximum pressure.	(2) Between ignition and flame reaching boundary of sphere on horizontal axis.	Difference between (1) and (2).
20·25	17·17	16·02	+1·15
25·05	9·10	9·08	+0·02
29·40	6·40	6·38	+0·02
39·90	4·56	4·56	±0·00
45·25	4·24	4·28	−0·04
50·10	4·51	4·50	+0·01
58·70	5·18	5·20	−0·02
69·30	11·61	11·16	+0·45
74·00	24·44	20·28	+4·16

It is clear from these results that with all mixtures save those in which the flame-front travelled very slowly (mixtures containing less than about 25% or more than about 65% of carbon monoxide) the moment of maximum pressure coincides, within less than half a millisecond, with the arrival of the flame-front at the boundary of the vessel. When the flame-front travels so slowly that its movement is affected by convection, it reaches the top of the vessel, and can be seen at the ends of the window along the horizontal diameter, whilst there is still a considerable volume of mixture in the lower part of the vessel through which it has not travelled. The pressure therefore continues to rise after the flame has reached the boundary of the sphere on its horizontal axis.

Explosions within a Cube.—By removing two shaped castings of phosphor-bronze from within the casing of the explosion-vessel, a cubical cavity of 15 cm. edge was produced, the arrangement of manometer diaphragm, firing electrodes, and horizontal window remaining the same as when the cavity was spherical, except that the window now had an effective width of 4 mm. In addition, the removal of the castings that had formed the spherical cavity uncovered a window 4 mm. wide, which passed diagonally from corner to corner across the face of the cube opposite to that in which the horizontal window was fitted. By an arrangement of interconnected chain-gearing, simultaneous photographs, on two revolving drums, could be taken of the flame-front as it moved from the centre of the cube (*a*) towards the walls and (*b*) towards the corners. The time–pressure chart was recorded only on the drum used for photographing the horizontal window.

Mixtures of carbon monoxide and air were used similar to those when the cavity was spherical. Typical records, obtained with a mixture containing 60% of carbon monoxide, are reproduced on Plate III (these are reduced in size, but not in the same proportion as for Plate II). When interpreting these records, the lenses of both cameras, which were focussed on the igniting spark, may be regarded as looking into the interior of the bomb from either side, the one through a horizontal and the other through a diagonal window.

Considering first the record obtained through the horizontal window (*a*, Plate III): The lens will "see" best of all the flame as it travels across a vertical plane through the spark-gap, on which the lens has been focussed. Nearer, and in less accurate focus, it will see the front edges of the two sides of the cavity. Farther away, and in better but not perfect focus, it will see the two-sided corners formed by the sides and back of the cavity. The two pairs of curved V-shapes on the record show the progress of the flame after it has reached the sides of the cavity and is travelling (the outer pair) towards the front corners and (the inner pair) towards the back corners.

In the photograph obtained through the diagonal window, the lens "sees" four three-sided corners and the record shows the times at which the flame reaches, (i) and (ii), the upper and lower near corners of the cube (the outer "horns" in the photograph), and (iii) and (iv), the upper and lower far corners (the inner horns).

Measurements obtained from series of photographs similar to those reproduced on Plate III are recorded in Table II. From these measurements it is apparent that pressure continues to be developed slowly after the flame-front has touched the walls of the cube and whilst it is squeezing itself into the corners.* Thus the moment of attainment of maximum pressure when the explosion-vessel is cubical does not synchronise exactly, even when ignition is central, with the moment of "complete inflammation" of the mixture, but is antecedent to it, no doubt because, whilst the flame-front at each of the eight corners is nearing the end of its journey, there is considerable cooling of the gases, burnt earlier during the explosion, at the faces of the cube.

A comparison of the time–pressure charts obtained with the same mixture (60% carbon monoxide in air) exploded in the two

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* The photographs reproduced on Plate II of our paper (J., 1925, **127**, 764) help to explain why this should be so.

TABLE II.

Explosions of Carbon Monoxide and Air within a Cube.
(*Mixtures Saturated with Water-vapour at* 19°.)

	Time-intervals, measured from time of ignition (in 1/100ths of a second).				
CO (%).	Attainment of maximum pressure.	Flame at sides (see *a*, Plate III).	Flame at two-sided corners (see *a*, Plate III).	Flame at top corners (see *b*, Plate III).	Flame at bottom corners (see *b*, Plate III).
20·30	22·86	6·7	19·75	21·36	25·25
30·20	7·78	4·9	6·84	8·28	8·58
40·20	6·04	4·0	5·32	6·49	6·56
45·20	5·70	3·9	4·98	6·13	6·13
50·00	6·09	4·2	5·40	6·46	6·69
60·40	8·64	5·7	7·65	9·39	9·78
69·55	25·02	10·2	20·64	22·44	27·50

shapes of vessel (see Plates II and III) brings out clearly the extent to which cooling occurs during the development of pressure when part of the flame-front can touch a cold metal surface whilst the remainder is still travelling through part of the mixture. It will be seen also that the character of the "cooling-curve" is affected by the shape of the explosion-vessel. In this connexion, we would emphasise our previous observation (*loc. cit.*, p. 767) that, when attempting to interpret the character of time–pressure curves obtained from gaseous explosions in closed vessels, due consideration must be paid to the shape of the vessels and to the position of the point of ignition.

This work forms part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

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[*Received, October* 15*th*, 1926.]

XXVII.—*Molecular Structure in Solution. Part I. The Densities and Viscosities of Aqueous Solutions of Cobalt Chloride and Hydrochloric Acid.*

By OWEN RHYS HOWELL.

THE red and blue colours of the cobaltous compounds and the change from one to the other have been the subject of many investigations. The latest work is that of Hill and Howell (*Phil. Mag.*, 1924, 48, 833), where a fairly full account of previous work will be found.

These authors examined the absorption spectra in the visible region of a number of cobaltous solutions and solid pigments. They showed that the spectra of the red solutions were precisely similar to those of the red pigments, and the spectra of the blue solutions to those of the blue pigments. In the *red* pigments, the cobalt atom replaced the atom of another metal known from *X*-ray examination of the crystal structure to be surrounded by *six* other atoms, whilst in the *blue* pigments it replaced an atom similarly known to be surrounded by *four* other atoms. The conclusion was therefore drawn that in the red solutions the cobalt atom is surrounded by six other atoms or groups, whilst in the blue solutions it is surrounded by four. The suggestion was made that a definite association of groups or a molecular structure exists in solution, just as in solids. Thus in the dilute aqueous solution of any cobaltous salt, which is red, the cobalt atom is in association with six water molecules, whilst in the blue solution of cobalt oxide in potash it is in association with four groups, possibly hydroxylic.

Support for this view is found in the work of French and Lowry (*Proc. Roy. Soc.*, 1924, *A*, **106**, 489). These authors examined the absorption spectra of a number of cupric salts in different solvents, and showed that they all consisted essentially of one band in the infra-red or red, which was due to the cupric atom, and another in the ultra-violet, which depended on the other part of the molecule. Since the cupric atom gives only one band (which, however, varies in position with the nature of the compound), the authors concluded that the cupric atom is similarly associated in all the solutions. Since many of the salts examined were the cupric salts of organic acids, which are known to be co-ordinated compounds, the conclusion was drawn that in solution the cupric atom is always associated with four other atoms or groups. Although many of the co-ordinated compounds are stable in aqueous solution, others are decomposed. The spectrum, however, is of the same type, and it is therefore concluded that in these solutions, and in dilute aqueous solutions of simple cupric salts, the cupric atom is surrounded by four molecules of water.

In the present paper, an account is given of work which throws further light on the existence of a molecular structure in solution. It deals with the change in colour from red to blue on adding hydrochloric acid to an aqueous solution of cobalt chloride. The densities and viscosities of a series of solutions, having the same concentration of cobalt chloride but increasing concentrations of hydrochloric acid, have been measured. The same properties for an exactly similar series of solutions without cobalt have also been evaluated, and from the differences in the values for corresponding solutions it is possible to follow the change which takes place in the state of the cobaltous atom. It is suggested that in the aqueous solution, the cobalt is present as hydrated ions, $Co(H_2O)_6^{\cdot\cdot}$, where the cobalt atom is surrounded by six groups, and that as the concentration of hydrochloric acid is increased, these are progressively converted into ions where the cobalt is surrounded by four groups, probably the complex ions, $CoCl_4''$. The existence of complex cobaltous ions in solution is discussed by Hantzsch and Shibata (*Z. anorg. Chem.*, 1912, **73**, 309) and by Kotschubei (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055).

EXPERIMENTAL.

Determination of Density.—The determination of the density of a liquid is more rapidly and conveniently made with an ordinary specific-gravity bottle than with a pyknometer. Carefully used, this bottle gives reproducible and accurate results. One source of error lies in replacing the stopper in different positions. This was avoided by making a small file mark on the neck of the bottle and on the stopper, and replacing the stopper for each determination so that the marks were in line. Another and more serious error is due to evaporation, which occurs, not only through the hole in the stopper, but more especially through the ground joint. Even when the hole in the stopper is effectively closed, there is a continuous loss in weight so long as the liquid in the bottle is in contact with any portion of the ground surfaces. It would appear that the liquid rises in the fine channels between the roughened faces, and thus reaches the outside round the stopper, where it evaporates. All evaporation is completely prevented by placing over the stopper and the neck of the bottle a small cap, made from glass tubing, which rests on the shoulders of the bottle. Protected in this way, a bottle full of aqueous solution remains unchanged in weight for many hours.

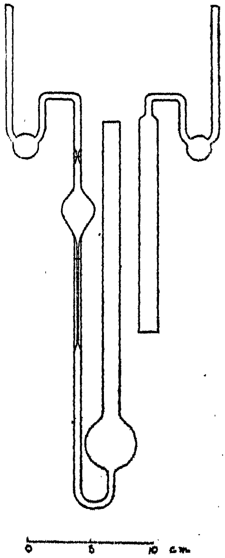
All determinations of density were made with a density bottle of about 25 c.c. capacity, the precautions described above being taken. The relative density was calculated from the formula

$$d^{20°}_{20°} = W'/W - 0{\cdot}0012(W' - W)/W,$$

where W = weight of water filling the bottle, W' = weight of solution filling the bottle, and $0{\cdot}0012$ = mean density of air. The maximum error in the determinations is less than one unit in the fourth place of decimals.

Determination of Viscosity.—The viscosity measurements were made in a viscometer of the Ostwald type. In order to provide against evaporation and loss of gas from the strongly acidic solutions (especially at the higher temperatures at which further measurements will be made), a simplified modification of the apparatus used by Findlay (*Z. physikal. Chem.*, 1912, **79**, 97) was specially made. The viscometer is shown in Fig. 1. It consists of two parts, one being precisely similar to the Ostwald viscometer. The volume of the upper bulb is about 10 c.c. and the diameter of the capillary about 0·4 mm. The narrow limb is continued to form a U-tube with a small bulb of about 2 c.c. capacity. The other part consists of a tube which just fits over the broad limb of the viscometer and is also provided with an exactly similar U-tube. The two parts are held together by a rubber band. This arrangement is simpler and more satisfactory than one having a ground joint as no lubricating material is employed and no contamination of the solution is possible.

FIG. 1.



The apparatus is easily taken apart for emptying and cleaning. It was initially thoroughly cleansed with chromic acid, and thereafter rinsed with distilled water after each experiment. It was dried by drawing through it a stream of air, filtered through cotton-wool and dried by concentrated sulphuric acid and calcium chloride. With this treatment alone, it was found that after several determinations concordant results ceased to be obtained and this was traced to the presence of grease. The apparatus was therefore also washed with a little pure alcohol or acetone, filtered while boiling.

A determination of viscosity was made as follows: The small bulbs on the U-tubes were about half-filled with the solution. A fixed amount (16 c.c.) of solution was pipetted into the viscometer. The two portions were assembled, and the apparatus was slipped into two clips fastened to a bar clamped upright in the thermostat. It was thus ensured that the apparatus was perfectly vertical for each experiment. The apparatus was immersed so that only the open ends of the U-pieces were above water. The solution in the small bulbs being under the same conditions as that in the apparatus, and all interchange of air having to take place through the bulbs, the solution under examination suffers no change in composition. It was found that perfectly concordant values were obtained for a large number of consecutive measurements or at long intervals.

The time of flow was measured by means of a stop-watch reading to $\frac{1}{5}$ of a second. The time for water was 376·6 seconds, and this was checked at intervals throughout the measurements and found to be exactly reproducible. All the solutions examined had a time of flow greater than this, so that the maximum error in the determinations of viscosity is less than about 0·05%. In calculating the viscosity coefficient, the value $\eta_{20^\circ} = 0{\cdot}01005$ for water was used.

Materials. The water used for determining the water constant of the viscometer and for making up the solutions was laboratory-distilled water, filtered, and twice re-distilled with precautions to preclude contamination by dust or grease. The hydrochloric acid was the pure commercial product, and the cobalt chloride was Kahlbaum's purest, free from iron and nickel.

Solutions. Two stock solutions were prepared, one containing 120 g. per litre of $CoCl_2,6H_2O$ in water, and the other containing the same amount per litre in concentrated hydrochloric acid. The acidity of this solution was found to be 10·63*N* by diluting and titrating against standard sodium hydroxide. From these two solutions a series of solutions was made, each having the same concentration of cobalt chloride, but varying concentrations of hydrochloric acid. This was done by taking x c.c. of the aqueous solution and $(50 - x)$ c.c. of the acid solution, and making up to 50 c.c. with water.

An exactly similar series of solutions containing the same amounts of acid as the foregoing, but no cobalt, was made in precisely the same way from water and a stock solution of hydrochloric acid of the same strength as above (10·63*N*).

Carefully graduated vessels were used in all cases and the error in composition does not exceed 0·1%. The volumetric handling of the solutions, necessitating the largest error in this work, consequently imposes the limit on the accuracy of the measurements of their densities and viscosities.

All measurements were made in a thermostat, with glass front and back, regulated to 20° ± 0·01°.

Results.

Densities.—The relative densities of the two series of solutions, determined as described, are given in Table I. Many previous determinations of the density of hydrochloric acid solutions have been made over a wide range of concentration (see, *e.g.*, Pickering, *Ber.*, 1893, 26, 277; Lunge and Marchlewski, *Z. angew. Chem.*, 1891, 4, 133; Lunge, "Technical Chemists' Handbook"). As most of these investigators have expressed their results as absolute densities ($d^{20^\circ}_{4^\circ}$), the values now found are also given in the same

TABLE I.

Densities.

1. Normality of acid, N.	2. Relative density of $CoCl_2 + HCl$, $d^{20°}_{20°}$.	3. Relative density of HCl alone, $d^{20°}_{20°}$.	4. Relative density (calc.).	5. Absolute density, $d^{20°}_{4°}$.	6. Density difference (2—3).
0	1·0582	1·0000	*1·0000*	*0·9982*	0·0582
1·063	1·0755	1·0186	*1·0182*	*1·0168*	0·0569
2·126	1·0926	1·0364	*1·0361*	*1·0346*	0·0562
3·189	1·1092	1·0536	*1·0536*	*1·0518*	0·0556
4·252	1·1261	1·0707	*1·0707*	*1·0689*	0·0554
5·315	1·1420	1·0871	*1·0874*	*1·0852*	0·0549
6·38	1·1575	1·1036	*1·1038*	*1·1016*	0·0539
6·59	1·1602	1·1067	*1·1070*	*1·1048*	0·0535
6·91	1·1639	1·1112	*1·1119*	*1·1093*	0·0527
7·23	1·1678	1·1162	*1·1167*	*1·1142*	0·0516
7·44	1·1704	1·1195	*1·1198*	*1·1176*	0·0509
8·50	1·1830	1·1355	*1·1355*	*1·1337*	0·0475
9·57	1·1957	1·1507	*1·1507*	*1·1488*	0·0450
10·63	1·2100	1·1657	*1·1656*	*1·1637*	0·0443

form in col. 5 of Table I for the sake of comparison. They agree closely with those already reported in the literature.

The values of the relative densities are plotted against the concentration of acid for the two series of solutions in Fig. 2A. It is seen that the curve for the solutions of acid only is a smooth one. As for most aqueous solutions, the relative density is expressed approximately by an equation of the form

$$d_{\text{solution}} = d_{\text{water}} + xN + yN^2,$$

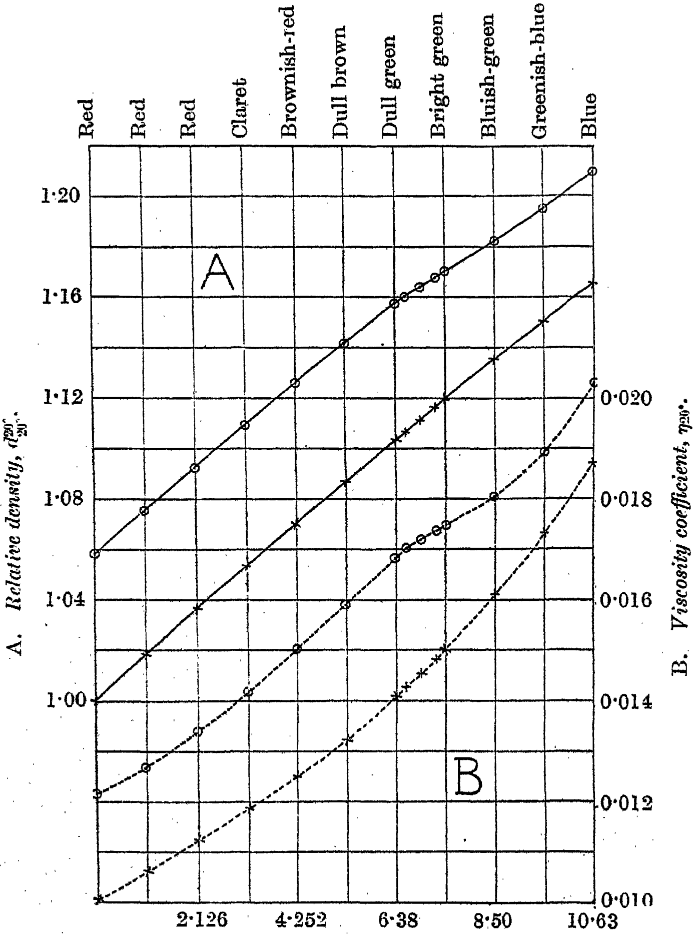
where x and y are constants, and N is the normality of the solution. Putting $x = 0·017321$ and $y = -0·00016316$, the values calculated from the expression are given in col. 4 of Table I. Comparing them with the observed values in col. 3, it is seen that the agreement is very fair throughout the range. Better agreement is not obtained by inserting a cubic term in the expression.

The curve for the solutions containing cobalt, on the other hand, is not smooth. It consists of two parts, one (for the lower values) being convex and the other concave to the line joining the extreme values. The break in the curve is obvious. It occurs after the maximum colour change, and this circumstance is discussed later.

Many measurements are on record showing breaks in density and viscosity curves, and theoretical conclusions have been drawn from such breaks alone. In the present instance, however, it is possible, not only to obtain more detailed and trustworthy evidence, but also to follow the course of the change which is the cause of the break.

By subtracting the values for the acid alone from the values for the solutions of cobalt chloride and hydrochloric acid the influence of the cobalt atom on the molecular structure of the solution is brought to light. If the arrangement of the atoms or groups around the cobalt atom were the same, whatever the concentration of acid present, the two curves should be parallel and the difference between

FIG. 2.



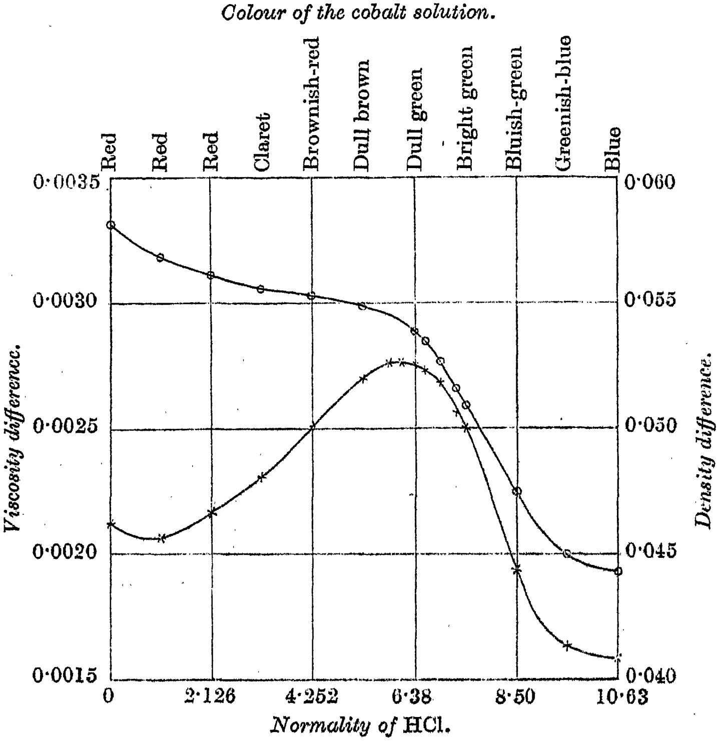
A. (*Full line curves*). *Relative density.*
B. (*Dotted line curves*). *Viscosity coefficient.*

Solutions of hydrochloric acid + cobalt chloride shown thus, ⊙.
Solutions of hydrochloric acid only shown thus, ×.

the values for corresponding solutions in the two series should evidently be constant.

These values are given in col. 6 of Table I, and are hereafter referred to as density differences, for brevity. It is seen that they vary continuously with the concentration of the acid. The differences are plotted against the concentration of acid in Fig. 3, and the curve can be fully interpreted in the light of the theory already given.

FIG. 3.



Upper curve : density differences.
Lower curve : viscosity differences.

In the aqueous solution, the cobalt chloride is largely ionised. The cobalt ions are hydrated with six molecules of water, and the solution is therefore red. As the solution is made increasingly acidic, this structure is broken down. The water molecules are crowded out by chlorine ions, and the cobalt atom becomes eventually surrounded by four chlorine atoms, the solution then being blue. Since the final value for the density difference is less than the initial value, the "four"-packing must be less dense than the "six." There should be a continuous diminution of the difference in density as the change proceeds from the red to the blue form, and this is seen to be so, for the curve falls along its entire course. When the change is complete, further increase in the concentration of acid should have no further effect, *i.e.*, the difference in density between the cobalt solution and one containing the same amount of acid only should become and remain constant. It is seen that this state has practically been reached at the highest concentration of acid employed, for the curve is rapidly flattening out to become parallel to the axis of hydrochloric acid concentration.

It is seen that the diminution of the difference in density, although continuous, does not take place evenly throughout the change from red to blue. The change is at first very gradual, and then (at a point corresponding to the abrupt change in the viscosity-differences curve, which will be discussed later) it takes place very rapidly. This also is explicable and is attributed to two causes.

First, as the change from the six- to the four-packing proceeds, the balance between the undissociated cobalt chloride and its ions is disturbed, and more salt therefore becomes ionised. The newly-liberated cobalt ions are immediately hydrated. The water used up for this purpose was previously free, but is now bound in close union with the cobalt atom, thus making the solution denser and counteracting the diminution due to the formation of the four- from the six-packing.

Secondly, and more important, is the effect of the electrical attraction between the ions. The $Co(H_2O)_6^{\cdot\cdot}$ ions present in the aqueous solution carry a double positive charge. The $CoCl_4''$ ions produced by the action of the acid carry a double negative charge. As the concentration of acid is increased, the amount of the negatively charged ion also increases. There will evidently be a great attraction between these oppositely charged ions. This will result in a closer association of the constituents of the solution, tending to make it more dense and thus counteracting the general diminution in density due to the looser packing of the four- than the six-grouping. This effect will continue to become more and more marked until the amounts of both ions present are the same, when the attraction between them will be a maximum. It is seen that, for the first part of its course, the curve does actually become increasingly less steep.

After one-half of the cobalt ions have undergone the change from the sixfold to the fourfold association, continued increase in the strength of the acid produces a far greater diminution in the density difference. The continued production of $CoCl_4''$ ions from the $Co(H_2O)_6^{\cdot\cdot}$ ions not only causes, in itself, a diminution of the density difference, but, whereas it formerly increased the attraction between the two kinds of ions by making their number more nearly equal, and thus tended to counterbalance the decrease in the density difference, it now makes the numbers of the two kinds of ions more and more unequal, thus lessening the attraction between them and causing the density difference to decrease far more rapidly. It is seen that the curve which begins by falling less and less steeply now falls extremely sharply.

It is therefore suggested that the point at which the curve undergoes inflexion corresponds (very approximately) to a solution having equal amounts of the two kinds of ions, *i.e.*, having equal numbers of cobalt atoms with the six- and four-groupings.

It is to be noted that this point does not correspond with the maximum colour change. The solution has already changed colour before the curve exhibits inflexion. This is in accordance with the fact already pointed out by Hill and Howell (*loc. cit.*) that the absorption spectra of blue cobalt solutions show that both forms (red and blue) may be present together. Thus the absorption spectrum of cobalt chloride in magnesium chloride solution clearly shows the presence of the red association although the solution appears quite blue. Indeed, since the blue form is far more intense than the red, the solution may have considerably more of the red form than of the blue, and still be perfectly blue to the eye. In the present instance, it is seen clearly that the colour change has already taken place before even half of the cobalt has changed from the six- to the four-association.

Viscosities.—The viscosity coefficients of the two series of solutions, determined as already described, are in Table II. Previous determinations of the viscosity of solutions of hydrochloric acid alone have been made by Reyher (*Z. physikal. Chem.*, 1888, **2**, 744), and of aqueous solutions of cobalt chloride alone by Wagner (*ibid.*, 1890, **5**, 31) and by Green (J., 1908, **93**, 2023).

The results given in Table II are plotted in Fig. 2B. It is seen that the values for hydrochloric acid lie on a perfectly smooth curve, which, however, cannot be even approximately represented by an expression of the type found to hold good for the density curve, or by one having a cubic term.

The curve for cobalt chloride and hydrochloric acid evidently consists of two distinct parts, both of which are concave to the line joining the extreme values. The break occurs at precisely the same concentration as that in the corresponding density curve, and is far more pronounced. If the cobalt atom were similarly associated in all these solutions, the two curves should be parallel, *i.e.*, the viscosity differences should be constant.

TABLE II.

Viscosities.

1. Normality of acid, *N*.	2. Viscosity coeff. of $CoCl_2$ + HCl, η_{20°.	3. Viscosity coeff. of HCl alone, η_{20°.	4. Viscosity difference (2—3).
0	0·01218	0·01005	0·00213
1·063	0·01272	0·01065	0·00207
2·126	0·01342	0·01125	0·00217
3·189	0·01418	0·01187	0·00231
4·252	0·01502	0·01251	0·00251
5·315	0·01593	0·01323	0·00270
* 5·85	0·01640	0·01364	0·00276
* 6·11	0·01662	0·01386	0·00276
6·38	0·01683	0·01408	0·00275
6·59	0·01703	0·01430	0·00273
6·91	0·01721	0·01452	0·00269
7·23	0·01738	0·01482	0·00256
7·44	0·01750	0·01500	0·00250
8·50	0·01805	0·01611	0·00194
9·57	0·01894	0·01731	0·00163
10·63	0·02028	0·01870	0·00158

* The values of the viscosity coefficients for these two concentrations are read from the viscosity curves shown in Fig. 2B.

It is seen, however, from the values of the viscosity differences, given in col. 4 of Table II, that they show a remarkable variation. The values are plotted against the normality of the acid in Fig. 3. The curve first exhibits a very small dip. The first effect of the acid on the solution is to decrease the ionisation of the cobalt chloride owing to the addition of a common ion. This results in a decrease of the number of cobalt ions present. These hydrated ions may reasonably be assumed to be comparatively highly viscous and the reduction in their number therefore leads to an initial decrease in the viscosity difference.

This initial effect of the acid is, however, soon overwhelmed by the increase in ionisation resulting from the transformation of the $Co(H_2O)_6^{\cdot\cdot}$ ions into $CoCl_4''$ ions by the action of the acid. The presence of these two kinds of ions, oppositely charged, causes an increase in the viscosity of the solution. Their electric fields, causing a strong attraction between them, retard their movement past one another, thus causing the solution to become more viscous. Increase in the concentration of the acid causes further transformation of the one type of ion into the other. The viscosity-differences curve therefore rises rapidly, and this in spite of the fact that the corresponding density curve is falling. As already noted when discussing the density changes, the attraction between the ions should be a maximum when there are equal numbers of each. It is seen that the curve rises to a maximum. It is suggested that at the maximum there are equal numbers of the two kinds of ions present, and it should be noted that the maximum in the viscosity-differences curve corresponds exactly with the point of inflexion in the density-differences curve, which was accounted for by the same reasoning.

Continued increase in the concentration of acid causes continued transformation of the cobalt atom from the six- to the four-packing. This results in the number of ions of each kind becoming increasingly unequal, in the attraction between them becoming thereby diminished, and therefore in the viscosity difference decreasing continuously. It is seen that the curve falls sharply from the maximum.

When the whole of the cobalt has assumed the new configuration, further increase in the concentration of the acid should produce no change in the viscosity difference. It is seen that, as with the density-differences curve, so also the viscosity-differences curve flattens out and indicates that, with the highest concentration of acid employed, the change to the four-configuration is practically complete.

It is also to be noted that whilst the density-differences curve indicates that the density of the four-configuration is less than that of the six-, the viscosity-differences curve shows that its viscosity is also less.

It is proposed to make further similar measurements at different temperatures and with different concentrations of cobalt, and also to determine other physical constants for these solutions.

Summary.

1. The densities and viscosities of a series of aqueous solutions containing a constant amount of cobalt chloride and varying amounts of hydrochloric acid have been determined.

2. The densities and viscosities of an exactly similar series containing hydrochloric acid only have also been measured.

3. From the differences in values for corresponding solutions, the effect of the acid on the cobalt in solution can be followed.

4. The curve showing the differences in density exhibits a point of inflexion, and that showing the differences in viscosity a maximum, both well-defined and at the same concentration of acid.

5. The general form of the curves and these two important characteristics are explained by attributing the action of the acid to the forcing of the cobalt atom out of its association with six molecules of water into an association with four atoms of chlorine.

6. The change of colour from red to blue and the point at which it occurs are accounted for.

The author would express his thanks to Prof. Alex. McKenzie, F.R.S., for giving him every facility for prosecuting this work.

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[*Received, October 4th*, 1926.]

XXVIII.—*The Interaction of Potassium* m-*Tolyloxide with Aliphatic Esters in Aqueous–Alcoholic Solutions.*

By ERNEST LESTER SMITH.

THIS research is an extension of the work of Gyngell (J., 1926, 2484; and private communication) on the interaction of potassium phenoxide with aliphatic esters in alcoholic solutions. The present reaction is shown to take the same course as the former: The water in the aqueous alcohol hydrolyses the potassium tolyloxide, with formation of cresol and potassium hydroxide; the latter then hydrolyses the ester. This hypothesis led to an expression for the velocity coefficient which was satisfactory within the limits of experimental error. Thus, we have

$$\underset{(c-x-y)}{CH_3{\cdot}C_6H_4{\cdot}OK} + \underset{(b-x-y)}{H_2O} \rightleftharpoons \underset{(d+x+y)}{CH_3{\cdot}C_6H_4{\cdot}OH} + \underset{y}{KOH}$$

$$\underset{(a-x)}{CH_3{\cdot}CO_2Et} + \underset{y}{KOH} \longrightarrow \underset{x}{CH_3{\cdot}CO_2K} + EtOH$$

where a, b, c, and d are the initial concentrations of ester, water, tolyloxide, and cresol, respectively, and x is the amount of potassium acetate formed and y the amount of free potassium hydroxide present at time t, the concentrations of the reacting molecules being as shown. For equilibrium

$$K(c-x-y)(b-x-y) = (d+x+y)y \quad . \quad . \quad (1)$$

where K is the equilibrium constant. For the second reaction

$$dx/dt = k(a-x)y \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

k being the velocity coefficient. It must now be assumed that y is always very small compared with x, *i.e.*, that the alkali formed by hydrolysis is always at a negligibly small concentration. Eliminating y, we obtain

$$dx/dt = Kk(a-x)(b-x)(c-x)/(d+x) \quad . \quad . \quad (3)$$

which on integration yields

$$Kk(t_2-t_1) = \frac{(d+a)}{(b-a)(c-a)}\log_e\frac{(a-x_1)}{(a-x_2)} + \frac{(d+b)}{(a-b)(c-b)}\log_e\frac{(b-x_1)}{(b-x_2)} + \frac{(d+c)}{(a-c)(b-c)}\log_e\frac{(c-x_1)}{(c-x_2)} \quad . \quad . \quad . \quad . \quad (4)$$

t_1 and x_1 corresponding to the earliest determinable time and titre, respectively, and t_2 and x_2 to subsequent determinations.

Simplification can be effected for two special cases: (*a*) When ester and tolyloxide are present in equivalent proportions, *i.e.*, $a = c$,

$$Kk(t_2 - t_1) = \frac{(d+a)(x_2-x_1)}{(b-a)(a-x_1)(a-x_2)} + \frac{(d+b)}{(b-a)^2}\log_e\frac{(b-x_1)(a-x_2)}{(b-x_2)(a-x_1)} \quad (5)$$

and (*b*) when, in addition, water is in such large excess as to be virtually constant,

$$Kk(t_2 - t_1) = \frac{(d+a)(x_2-x_1)}{b(a-x_1)(a-x_2)} - \frac{1}{b}\log_e\frac{(a-x_1)}{(a-x_2)} \quad . \quad (6)$$

The reaction between potassium *m*-tolyloxide and ethyl acetate proceeded somewhat more rapidly than that with potassium phenoxide under the same conditions. On application of formula (5), with $x_1 = 0$, $t_1 = 0$, values were obtained for *Kk* which were sensibly constant. Further experiments, in which the concentrations of the reactants and also the temperature have been varied between wide limits, have yielded values for *kK* in which the maximum deviation from the mean usually lies between 2 and 5%; this can be ascribed to experimental error, since the deviations are irregular.

The following experiment is typical, time being expressed in minutes and concentrations in milliequivs. per litre.

TABLE I.

Potassium *m*-tolyloxide, *N*/2. Temperature 70°.
Ethyl acetate, *N*/2. Water = 10% of total.

Time.	Titre.	% Reaction.	x.	$a - x$.	$b - x$.	$Kk \times 10^6$.
0	20·0	—	—	500	5555	—
5	15·3	23·5	117·5	382·5	5438	—
19	11·75	41·2	206	294	5349	1·64
35	9·95	50·2	251	249	5304	1·65
41	9·6	52·0	260	240	5295	1·58
54	8·65	56·8	284	216	5271	1·64
87	7·25	63·8	319	181	5236	1·62
119	6·3	68·5	342·5	157·5	5213	1·63
125	6·25	68·8	344	156	5211	1·60
					Mean	1·62

The reaction is evidently similar to that investigated by Gyngell (*loc. cit.*). No trace of the *m*-tolyl ether could be detected among the products of reaction. Further, if it proceeded in any way different from that assumed, it is extremely unlikely that constant values for *Kk* would be obtained from the above formula. For example, it can be shown that any side reaction, occurring to the extent of 1—2% during the course of an experiment, would suffice to make Kk increase or decrease to the extent of about 10% during the run.

The reciprocal of the time for half-reaction was plotted against water concentration for several series of experiments. In each case, the curve was found to cut the water axis at a point corresponding to a water concentration of half that of the ester and tolyloxide, indicating that the time for half-reaction is infinite for water concentrations below this amount; this result is confirmed by the fact that reaction ceases when the water is entirely consumed.

Tables II, III, IV, and V show the values of Kk obtained with the four esters examined. In the last three tables, the concentration of both the ester and the tolyloxide was $N/4$.

TABLE II.

Reaction with ethyl acetate.

% Water.	Tolyloxide.	Ester.	$Kk \times 10^6$.	
0·27	$N/2$	$N/2$	2·55	
1	,,	,,	2·48	
2·5	,,	,,	2·31	
2·5	,,	,,	2·29	Excess cresol = $N/8$.
2·5	,,	,,	2·48	Excess cresol = $N/4$.
5·2	$N/4$	$N/4$	1·92	
5	,,	,,	1·21	Temp. 64·9°.
5	,,	,,	0·84	Temp. 60·1°.
5	$N/8$	$N/2$	1·70	
5	$N/4$	,,	1·82	
5	$N/2$	,,	2·00	
5	,,	N	1·97	
5	,,	$N/4$	1·98	
7·5	,,	$N/2$	1·85	
9	,,	,,	1·65	
10	,,	,,	1·62	
12	,,	,,	1·50	
15	,,	,,	1·37	
20	,,	,,	1·26	
30	,,	,,	1·17	
100	$N/8$	$N/8$	0·880	
100	,,	,,	0·0240	Temp. 30°.
100	,,	,,	0·0149	Temp. 25°.

TABLE III.

Reaction with *n*-butyl acetate.

% Water ...	1·1	2·7	5·0	7·7	10·0	20·0	30·0	45·0
$kK \times 10^6$ ...	1·23	1·22	1·08	1·04	1·041	0·783	0·652	0·525

TABLE IV.

Reaction with *n*-propyl acetate.

% Water	1	2·5	5	10	15	20
$kK \times 10^6$	2·10	1·90	1·67	1·445	1·265	1·13

TABLE V.

Reaction with methyl acetate.

% Water	1	2·5	5	7·5	10	15	25
$kK \times 10^6$	1·91	1·605	1·40	1·34	1·29	1·31	1·33

Relative Activity of the Esters.—It was to be expected that the values of kK for the different esters would be in the order of their molecular weights, since the esters employed are members of an homologous series. As shown by the tables, however, methyl acetate is abnormal for low percentages of water.

Evaluation of Equilibrium Constant.—The constants obtained are the product of an equilibrium constant and a velocity coefficient. It is obviously desirable to determine the magnitudes of these separately if possible. A method by which this might be achieved, for the reaction in aqueous solution, was the comparison of the rates of hydrolysis of an ester by potassium tolyloxide and by potassium hydroxide, respectively. In the second case, k can be obtained directly, and by substituting this in the value for kK from the first experiment, it is evident that K can be calculated.

Preliminary experiments indicated that the reaction between potassium hydroxide and ethyl acetate was half completed in about 1 minute in the concentrations used, *viz.*, $N/8$ at 30°. As it was desirable to carry out the experiment under these conditions, a special apparatus was designed for the purpose, which is described in the experimental section. The bimolecular coefficients obtained show a maximum deviation from the mean of only 2·5%. The results are as follows:

Concentrations, $N/8$ in aqueous solution. Temperature, 30°. $kK = 0{\cdot}024 \times 10^{-6}$; $k = 0{\cdot}0086$; therefore $K = 2{\cdot}80 \times 10^{-6}$.

A further method by which the value of the equilibrium constant in aqueous solution has been found is by electrometric measurement of the hydrogen-ion concentration in solutions of potassium *m*-tolyloxide. The *E.M.F.* between a hydrogen electrode, immersed in a $N/8$-solution of potassium *m*-tolyloxide, and a saturated calomel electrode was measured by a potentiometer in the usual way. As the p_H is largely affected by a slight excess of either *m*-cresol or potassium hydroxide in the solution, the following procedure was adopted: To the solution were added a few c.c. of potassium hydroxide solution, and the mixture titrated until acid, using a microburette. The curve showed two breaks as anticipated. The first corresponds to the point where cresol and alkali are present in equivalent amounts, and the second more pronounced break to the point where all the alkali has been neutralised. The position of the first break was fixed by a cusp on the first differential curve. K

could have been calculated from the voltage at the equivalent point, so found, but for various reasons it was considered preferable to make use of a comparison method. Accordingly, the experiment was repeated, adding $N/10$-potassium hydroxide to $N/8$-potassium chloride solution. The ionisation of the former can be considered the same in solutions of potassium chloride or tolyloxide of the same strength; the alkali concentration is therefore the same in the two solutions when the *E.M.F.* is the same. Hence K can readily be calculated. The results are as follows:

Percentage hydrolysis of potassium *m*-tolyloxide	2·8%.
Equilibrium constant, K,	$1{\cdot}6 \times 10^{-6}$.

These experiments were carried out at 14·5°. Applying the temperature coefficient to the value for K obtained by the previous (kinetic) method, the value at 14·5° is calculated to be $1{\cdot}55 \times 10^{-6}$.

Both these methods appear to be of general application for the determination of the hydrolysis constants of the salts of very weak acids. The dynamical method is probably the more accurate. This value cannot, however, be applied to alcoholic solutions with any certainty, owing to "solvent effect," and it has not been found possible to determine K for alcoholic solutions. The comparison of the rates of hydrolysis of an ester by potassium tolyloxide and by potassium hydroxide is of no value on account of the potassium hydroxide–ethoxide equilibrium, for which the value of the equilibrium constant is at present unknown. Electrometric methods are equally inapplicable.

It will be seen from the tables that in aqueous-alcoholic solutions the value of the composite constant kK decreases with increase in the water concentration. It is, however, impossible to state whether this is due to variation of the velocity coefficient, of the equilibrium constant, or of both.

Alcoholysis of Potassium m-*Tolyloxide*.—In aqueous–alcoholic solutions of potassium *m*-tolyloxide, it is very probable that a certain amount of potassium ethoxide is present in equilibrium with the other components. It can be shown that the extent of this alcoholysis must be very small, since otherwise a more complicated formula would be required in order to give satisfactorily constant values for kK.

Temperature Coefficients.—It can be shown that the value of Q in the Arrhenius equation is the sum of the values for the two reactions:

$$\log_e K_1/K_2 = Q_1(1/T - 1/T')/R$$
$$\log_e k_1/k_2 = Q_2(1/T - 1/T')/R$$

Adding,

$$\log_e k_1K_1/k_2K_2 = (Q_1 + Q_2)(1/T - 1/T')/R$$

The temperature coefficient in alcoholic solution with 5% of water has been measured with the following results:

TABLE VI.

Ethyl acetate, *N*/4. Potassium *m*-tolyloxide, *N*/4.

Temp.	$kK \times 10^6$.	$Q_1 + Q_2$.
60·1°	0·84	17,000
64·9	1·21	16,900
70·0	1·76	
		Mean 16,950

Ratio for 10° rise, 2·1.

The temperature coefficient in aqueous solution has also been measured:

TABLE VII.

Ethyl acetate, *N*/8. Potassium *m*-tolyloxide, *N*/8.

Temp.	$kK \times 10^6$.	$Q_1 + Q_2$.
25·1°	0·0149	17,200
30·0	0·0240	18,500
70·0	0·880	

Q_2, the value of Q for the hydrolysis of ethyl acetate by potassium hydroxide in aqueous solution, has been determined previously. Its value over the range 25—35° is 10,900 calories. If this number be subtracted from the value of $Q_1 + Q_2$ above, for the same range, the result will be Q_1. Hence $Q_1 = 6{,}300$ calories.

Reaction with Other Esters.—Gyngell (*loc. cit.*) has shown that certain esters, notably methyl and ethyl oxalates, react with potassium phenoxide differently from those of the methyl acetate series, giving rise to the corresponding phenyl ether in the same way as the alkyl iodides. The reaction between potassium *m*-tolyloxide and ethyl oxalate in dry alcoholic solution has been investigated. A liquid was obtained identical in properties with *m*-tolyl ether, prepared in the usual way.

Ethyl tartrate and ethyl and propyl formates have also been used. These esters react normally, but more than one hundred times as rapidly as ethyl acetate. After the water in the alcohol has been consumed, a very slow reaction appears to continue, with formation of the tolyl ether. In these cases, the yield was very small, rendering identification difficult.

Gyngell has suggested that the only esters with which this ether formation occurs are those in which no α-hydrogen atom is present. It is, however, difficult to understand how the mere absence of a group can cause a reaction to proceed, or how its presence can inhibit a reaction in which the group concerned takes no part. Moreover, formic and tartaric esters contain one α-hydrogen atom.

A fact much more likely to influence their reactivity is that these esters are all derived from relatively strong organic acids. This suggestion brings these esters into line with those of the common inorganic acids, which all appear to yield the ether readily and are all derived from very strong acids.

Reaction with Ethyl Monochloroacetate.—Monochloroacetic acid is one of the strongest organic acids, and, moreover, it has two α-hydrogen atoms. It therefore seemed of special interest to investigate the behaviour of its ethyl ester with potassium *m*-tolyloxide. The substances reacted very rapidly in dry alcoholic solution, but the main product proved to be a new ester, *ethyl* m-*tolyloxyacetate* :

$$CH_2Cl{\cdot}CO_2Et + C_7H_7{\cdot}OK \longrightarrow KCl + C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CO_2Et.$$

At the same time, a small quantity of the tolyl ether appeared to be formed.

Ethyl *m*-tolyloxyacetate does not appear to have been described previously, although the corresponding acid and some of its other compounds are mentioned by Beilstein. The ester is a colourless, oily liquid with a peculiar characteristic smell; b. p. 264°, with slight decomposition.

EXPERIMENTAL.

Alcohol was dried by refluxing with quick-lime for a few days. During the earlier part of this work, alcohol so treated was deemed to be dry, but later the remaining water was estimated by a method devised by the author, which it is hoped to publish shortly.

Potassium *m*-tolyloxide was prepared in solution only; potassium metal, rapidly freed from oil between filter papers, was added to alcohol under reflux, and the equivalent of *m*-cresol then added. This method of preparing such compounds has been justified by Robertson and Acree (*Amer. Chem. J.*, 1913, 49, 474) and by Cox (J., 1918, **113**, 670).

In all cases, the desired amount of water was added to the ester solutions, prepared as required. The reaction was carried out in a series of gas-heated thermostats regulated to ± 0·05° by means of mercury-filled thermo-regulators. The reaction vessels consisted of hard-glass test-tubes of about 15 c.c. capacity closed by rubber stoppers. In most cases, 5 c.c. of each solution were pipetted separately into each tube. After shaking, the tubes were transferred to the thermostat and withdrawn at suitable intervals of time, the contents being titrated with standard hydrochloric acid.

The Titration.—The accurate titration of the reaction mixture presents a problem of some difficulty. The mixture consists of alcohol, unchanged ester, free cresol, and potassium acetate and tolyloxide. The last two substances are salts of a strong base and a weak acid, so that both will be hydrolysed in solution, although to a different extent. In titrating the solution in the usual way, we are treating the potassium tolyloxide as an alkali and the potassium acetate as a neutral salt. Neither assumption is strictly correct. If a solution of the two salts, together with excess alkali, is titrated electrometrically, a curve will be obtained which shows three breaks, corresponding respectively to neutralisation of the free base, of that in the potassium tolyloxide, and of that in the potassium acetate. Consequently, the breaks cover a smaller range of p_H and are much less sharp than in an ordinary titration, and the choice of a suitable indicator is important. The problem is further complicated by the fact that the amount of potassium tolyloxide is decreasing, and potassium acetate increasing, throughout a run. It has been calculated that in a typical experiment the p_H value at the end-point varies from about 6 initially to 8 at three-quarter reaction, the end-point becoming progressively less sharp as the reaction proceeds. Since it is preferable to use the same indicator throughout, it is best to choose one which changes at p_H 7—8. This condition is satisfactorily fulfilled by litmus, provided that the bluish-violet colour is taken to indicate the end-point. These considerations are completely borne out in practice. Litmus is the only indicator, apart from lacmoid, which has been found satisfactory, others changing colour slowly and not at the true end-point.

Measurement of Rapid Reactions.—A simple apparatus was devised for this purpose consisting of a hard-glass boiling tube, with a smaller tube inside of about 12 c.c. capacity. The outer tube was closed by a rubber stopper to which was affixed a piece of stiff wire, bent at the end, which held the inner tube in position. 10 C.c. of one solution were delivered into the inner tube, and 10 c.c. of the other into the outer tube. After being heated in the thermostat for about 15 minutes, the apparatus was inverted once or twice to mix the solutions, then rapidly replaced in the thermostat. After the desired time, the contents were quickly poured into 20 c.c. of cold water containing nearly sufficient acid to neutralise the remaining alkali, the tubes rinsed out, and the titration was completed. By this means, the time error was probably not more than 2 or 3 seconds.

Summary.

1. The velocity of reaction between potassium *m*-tolyloxide and certain aliphatic esters in aqueous–alcoholic solutions has been investigated.

2. It is found that an equilibrium is established between potassium tolyloxide, water, cresol, and potassium hydroxide; the ester is hydrolysed by the last substance.

3. Constants are calculated which are the product of an equilibrium constant and a velocity coefficient.

4. The equilibrium constant in aqueous solution has been evaluated by two methods.

5. The temperature coefficient has been measured in both aqueous and alcoholic solutions.

6. It is found that esters of strong organic acids react very rapidly as above, and they also slowly form the corresponding *m*-tolyl ether.

7. A new ester, ethyl *m*-tolyloxyacetate, is described.

The author wishes to express his thanks to Dr. Crocker for suggesting the line of the research and for his continued interest therein, and to the London County Council for a grant which has enabled the research to be undertaken.

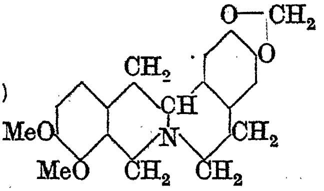
CHELSEA POLYTECHNIC, S.W. [*Received, July 15th,* 1926.]

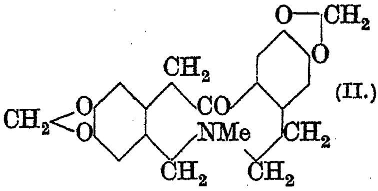
XXIX.—*Synthetical Experiments on Protopine and Allied Alkaloids. Part I.*

By THOMAS STEVENS STEVENS.

THE present investigation was undertaken with the object of elaborating methods for the production of the ten-membered ring of cryptopine, protopine, and related alkaloids by a direct ring-closure, without previous formation of a structure of the type of tetrahydroberberine (I) (compare Haworth and Perkin, J., 1926, 445, 1769). The synthesis of the isomeride (II) of protopine was first projected, on account of the accessibility of suitable initial materials, and this communication deals with attempts to bring about ring-closure between the carbonyl group and the adjacent benzene nucleus.

(I.)

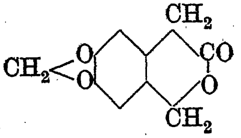


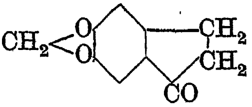


(II.)

Homopiperonylic acid condenses readily with formaldehyde to give the *lactone* (III) of 6-hydroxymethylhomopiperonylic acid, which was employed as the initial material for the "left-hand half" of the molecule (II). The constitution of this lactone was established by oxidation with permanganate, whereby it was converted into the methylenedioxyhomophthalic acid obtained by Perkin and Robinson (J., 1907, **91**, 1086) from 5 : 6-methylenedioxy-1-hydrindone (IV), which latter gives hydrastic acid on oxidation. In the first series of experiments, the lactone was converted by ammonia

(III.)

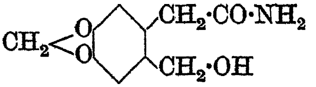


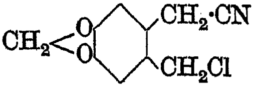


(IV.)

into 6-*hydroxymethylhomopiperonylamide* (V), and the amide treated with phosphorus trichloride, giving 6-*chloromethylhomopiperonylonitrile* (VI). By condensing this nitrile with *N*-methyl-β-piperonylethylamine, N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VII) was obtained, but attempts to convert this into (II) by an intramolecular Hoesch reaction were unsuccessful, only the corresponding *amide* being produced.

(V.)

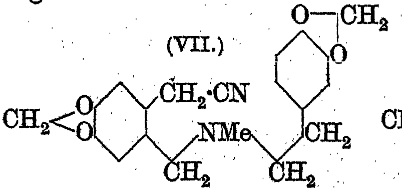




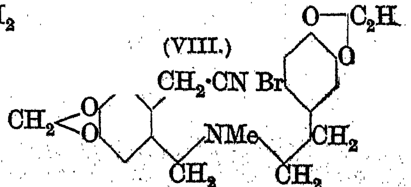
(VI.)

N-Methyl-β-piperonylethylamine is readily monobrominated in the 6-position, as is shown by the preparation of an identical product from 6-bromo-β-piperonylpropionamide (Haworth, Perkin, and Stevens, J., 1926, 1764) by treatment with sodium hypochlorite followed by methylation of the resulting 6-bromo-β-piperonylethylamine. The nitrile (VI) reacts with N-*methyl*-6-*bromo*-β-*piperonylethylamine*, giving N-*methyl*-N-6′-*bromo*-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VIII). It was not found possible to close the 10-membered ring, producing the substance (II), by an internal Grignard reaction involving the bromine atom and the nitrile group. As the material was invariably recovered unchanged, and therefore no organomagnesium compound was formed, it did not seem likely that better results would be obtained by preparing the ester corresponding to the nitrile (VIII), and attempting a similar ring-closure.

(VII.)

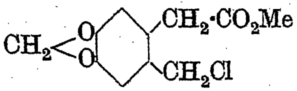


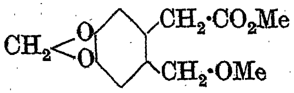
(VIII.)



It was hoped that successive treatment with phosphorus trichloride and methyl alcohol would convert the lactone (III) into methyl 6-chloromethylhomopiperonylate (IX), but only the *methoxy-ester* (X) was obtained. This result provides a striking illustration of the mobility of the halogen in the methylenedioxybenzyl halides; the isomeric 6-β-chloroethylpiperonoyl chloride (XI), in which the halogen is one position farther removed from the benzene nucleus, is smoothly converted into the corresponding chloro-ester (Perkin, J., 1890, **57**, 1032). The methoxyl group in methoxymethylhomopiperonylic acid is removed with remarkable ease: warming with dilute hydrochloric acid on the steam-bath rapidly converts the acid into the lactone (III). In the same way homopiperonyl methyl ether (Greene and Robinson, J., 1922, **121**, 2194) was found to give 2 : 3 : 6 : 7-bismethylenedioxy-9 : 10-dihydroanthracene (XII), which is known to be produced from homopiperonyl alcohol under experimental conditions similar to those employed (compare Ewins, J., 1909, **95**, 1486; G. M. Robinson, J., 1915, **107**, 270).

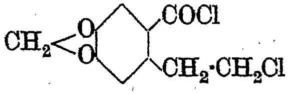
(IX.)

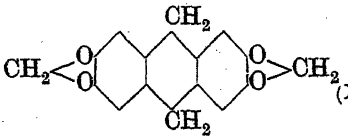




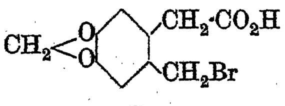
(X.)

(XI.)

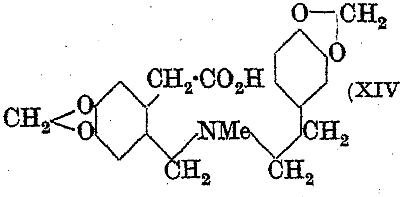




(XII.)



(XIII.)



(XIV.)

By treatment with hydrogen bromide, the substance (III) is converted into *6-bromomethylhomopiperonylic acid* (XIII), which is reconverted into the lactone by primary or secondary bases but readily forms the *methyl* ester with diazomethane. This ester yields N-*methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylic acid* (XIV) on condensation with *N*-methyl-β-piperonylethylamine and subsequent hydrolysis. It was not found possible to transform this into the compound (II) by conversion into the acid chloride and treatment with aluminium chloride.

EXPERIMENTAL.

Homopiperonylic Acid.—Much of the homopiperonylic acid used in this investigation was prepared by the following method, which is more convenient and much cheaper than that described by Buck and Perkin (J., 1924, **125**, 1679). Ethyl 3 : 4-methylenedioxymandelate (Barger and Ewins, J., 1909, **95**, 554), when boiled with 5—10% sodium hydroxide solution (10 parts), dissolves at once; the acid is obtained from the cooled and acidified solution : the troublesome hydrolysis with alcoholic alkali described by these authors is unnecessary. The acid (50 g.) is dissolved in acetic acid (500 c.c.) at 50—60°, and dry hydrogen bromide (50 g.) passed in. After 2 hours, the piperonylbromoacetic acid (not isolated) is reduced by addition of zinc dust (50 g.). The mixture is heated for 1½—2 hours on the steam-bath, hydrochloric acid (200 c.c.) added, and, when reaction ceases, the solution is filtered and cautiously diluted with water. Most of the homopiperonylic acid crystallises on standing, and a further quantity is obtained by extraction with chloroform. Yield, 75%.

Lactone of 6-Hydroxymethylhomopiperonylic Acid (III).—Homopiperonylic acid (10 g.), dissolved in hot acetic acid (30 c.c.), is mixed with hydrochloric acid (10 c.c.) and formalin (10 c.c. of 40%) and heated on the steam-bath for 45 minutes. The mixture is poured into water, extracted with chloroform, and the extract concentrated after being washed with sodium bicarbonate solution. The *lactone* separates on cooling and crystallises from alcohol in colourless leaflets, m. p. 137° (Found : C, 62·8; H, 4·2. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%). It is readily soluble in chloroform, less soluble in alcohol or benzene, very sparingly soluble in hot water, and almost insoluble in light petroleum. Cold sodium carbonate solution has no action on the lactone, but this dissolves readily in warm sodium hydroxide solution, and rapidly separates unchanged in the crystalline condition on acidification.

4 : 5-*Methylenedioxyhomophthalic Acid*.—To a solution of the lactone (2 g.) in warm dilute sodium hydroxide solution kept at 30—40°, potassium permanganate (3 g.), in aqueous solution, is gradually added. The mixture is treated with sulphur dioxide, concentrated, and strongly acidified; the acid then rapidly crystallises. It is freed from any unchanged lactone by solution in sodium carbonate and reprecipitation, and recrystallised from acetic acid, being obtained in small, colourless prisms, m. p. about 240° (decomp.). Perkin and Robinson (*loc. cit.*) give 236° (decomp.) (Found : C, 53·3; H, 3·7. Calc. for $C_{10}H_8O_6$: C, 53·6; H, 3·6%). The isomeric 3 : 4-methylenedioxyhomophthalic acid melts at 203—204° (decomp.) (Haworth, Perkin, and Stevens, *loc. cit.*). More drastic treatment of the lactone with permanganate, in the hope of obtaining hydrastic acid, gave oxalic acid as the only isolable product; further experiments on its oxidation, which are still in progress,

have led, among other results, to the indirect conversion of the lactone (III) into hydrastic acid, thus confirming the constitution assigned to it.

6-*Hydroxymethylhomopiperonylamide* (V).—The lactone (III) (10 g.) is dissolved in hot alcohol (80 c.c.), mixed with ammonia (250 c.c.; *d* 0·880), and warmed on the steam-bath for ½ hour. The solid which separates soon redissolves, and the *amide* (7 g.) crystallises on cooling. It forms fine, white needles from water or alcohol; m. p. 164—167° (Found: C, 57·7; H, 5·5; N, 6·5. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%). The substance is readily soluble in hot water or alcohol, very sparingly soluble in chloroform or benzene, and decomposes above its m. p. with evolution of ammonia and regeneration of the original lactone. It is readily hydrolysed by boiling with sodium carbonate solution.

6-*Chloromethylhomopiperonylonitrile* (VI).—Hydroxymethylhomopiperonylamide (10 g.), chloroform (50 c.c.), and phosphorus trichloride (15 c.c.) are boiled for 3 hours. The amide changes to an insoluble syrup, which is slowly converted into a yellow solid. The liquid is decanted cautiously into cold water, and the residue washed with chloroform and dissolved by agitation with successive small quantities of acetone, finally with addition of sodium bicarbonate solution. After filtering, the united liquors are extracted with chloroform, the extract is washed with sodium bicarbonate, dried, and evaporated, and the residue extracted repeatedly with light petroleum. The *nitrile* separates on cooling in long, colourless needles, m. p. 83—85°, which are very soluble in benzene, but rather sparingly soluble in light petroleum (Found: C, 56·9; H, 4·2; Cl, 17·3. $C_{10}H_8O_2NCl$ requires C, 57·3; H, 3·8; Cl, 16·9%).

N-*Methyl*-β-*piperonylethylamine* was prepared by Decker and Becker's method (*Annalen*, 1913, **395**, 335), piperonylidene-β-piperonylethylamine (Decker and Becker, *ibid.*, p. 349), which crystallises more readily and gives a purer product, being used instead of the benzylidene derivative.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VII).—The nitrile (VI) (1 g.) is boiled for 12 hours in benzene solution with methyl-β-piperonylethylamine (2·6 g.), and the liquid shaken with dilute hydrochloric acid (10 c.c. of 2*N*), a brown resin forming. The acid layer is separated, the resin and benzene are repeatedly extracted with hot water, and the united washings and acid layer are treated with concentrated hydrochloric acid, which precipitates the hydrochloride of the product as a gum. The liquid (containing the excess of methyl-β-piperonylethylamine) is decanted, the gum decomposed by ammonia, and the base extracted with chloroform and recrystallised from light petroleum. It forms fine, white needles, m. p. 74—76°, giving a violet solution in warm concentrated sulphuric acid (Found: C, 68·5; H, 5·9; N, 7·9. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 8·0%). The *nitrate* forms minute crystals, m. p. *ca.* 150° with effervescence, which are very sparingly soluble in cold water and almost insoluble in cold dilute nitric acid.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylamide*.—The base (VII) (0·6 g.) was mixed with dry ether (30 c.c.) and powdered zinc chloride (2·4 g.), stirred, cooled to —20°, and saturated with dry hydrogen chloride. After 12 hours, the mixture was again cooled and saturated with hydrogen chloride, and on the following day it was cautiously poured into water and heated until the ether had evaporated and no more of the gum would dissolve. Ammonia was added, and the base extracted with chloroform and recrystallised from methyl alcohol; it then formed small, white needles, m. p. 140°, very soluble in chloroform or hot methyl alcohol, which gave a violet solution in strong sulphuric acid and were not noticeably attacked by boiling for a short time with strong alkali. Analysis showed it to be the *amide* as stated, not the desired substance (II) [Found: C, 64·8; H, 6·0. $C_{20}H_{22}O_5N_2$ requires C, 64·9; H, 5·9%. $C_{20}H_{19}O_5N$ (II) requires C, 68·0; H, 5·4%]. The same amide is obtained when the substance (VII) is warmed for some time in methyl-alcoholic solution with excess of alkali and 2% hydrogen peroxide. The *picrate* crystallises from methyl alcohol in minute, orange-yellow plates, m. p. 210° (decomp.) after previous softening. Attempts to bring about the intended ring-closure under other conditions, including the use of aluminium chloride as condensing agent, gave no better result.

6-*Bromo*-β-*piperonylethylamine*.—(a) β-Piperonylethylamine hydrochloride is dissolved in water, and a slight excess of bromine, diluted with a little acetic acid, gradually added. The mixture is rendered strongly alkaline, and the oily base is washed by decantation, dissolved in a moderate excess of 2*N*-hydrochloric acid, boiled with charcoal, and concentrated hydrochloric acid added; the hydrochloride of the brominated base soon separates in nearly colourless prisms. The washings from the crude base yield a further small quantity on extraction with benzene, in which the substance is too sparingly soluble for the main portion to be extracted.

(b) 6-Bromo-β-piperonylpropionamide (Haworth, Perkin, and Stevens, *loc. cit.*) (5 g.) is finely powdered and heated to 70° with a solution prepared by passing the chlorine from potassium permanganate (1·2 g.) and excess of hydrochloric acid into aqueous sodium hydroxide (40 c.c. of 10%). After 2 hours, the aqueous layer is decanted, the oil extracted with hot dilute hydrochloric acid, and the cold filtered solution treated with potassium iodide. The hydriodide which is precipitated, and the benzoyl derivative prepared from it, were shown by mixed m. p. determinations to be identical with those made from the base obtained by process (a); the yield by method (b) is rather poor.

The *hydrochloride* dissolves readily in hot water or alcohol and gives a claret-coloured solution in concentrated sulphuric acid; it melts at 208—210° after sintering and losing its water of crystallisation at 110—120° (Found : C, 36·1; H, 4·3. $C_9H_{10}O_2NBr,HCl,H_2O$ requires C, 36·2; H, 4·4%. 0·1234 gave 0·1382 silver halides. Theory demands 0·1371). The base is a colourless oil, which could not be made to solidify, and absorbs carbon dioxide from the air. The *hydriodide* forms white microcrystals, m. p. 221°, which are fairly easily soluble in water, but much less soluble in potassium iodide solution. The *benzoyl* derivative is prepared in the usual manner and crystallises from methyl alcohol in fine, white needles, m. p. 138—140° (Found: C, 55·4; H, 4·3; Br, 23·3. $C_{16}H_{14}O_3NBr$ requires C, 55·2; H, 4·0; Br, 23·0%).

Piperonylidene-6-bromo-β-piperonylethylamine.—A solution of bromo-β-piperonylethylamine hydrochloride in hot alcohol is rendered just alkaline to phenolphthalein by alcoholic sodium ethoxide and filtered from sodium chloride, a slight excess of piperonal is added, and the mixture boiled for 2 hours. The Schiff's base crystallises on cooling in colourless prisms, m. p. 108—112° (Found: C, 53·9; H, 3·8; N, 3·7. $C_{17}H_{14}O_4NBr$ requires C, 54·3; H, 3·7; N, 3·7%).

N-*Methyl-6-bromo-β-piperonylethylamine.* — (a) Piperonylidene-bromopiperonylethylamine (5 g.) is heated with methyl iodide (3 c.c.) for 5 hours at 100° and the product is dissolved in 90—95% alcohol and boiled for 10 minutes. The hydriodide, which separates on addition of ether, is recrystallised from alcohol–ethyl acetate. In several experiments, apparently carried out under the usual conditions, a considerable quantity of a sparingly soluble salt was obtained, which crystallised from water in white needles, m. p. 260°, behaved like the iodide of a quaternary base, and would appear to be trimethyl-6-bromo-β-piperonylethylammonium iodide (Found: C, 34·6; H, 4·1. $C_{12}H_{17}O_2NBrI$ requires C, 34·8; H, 4·1%). The *picrate* crystallises from alcohol in minute, bright yellow plates, m. p. 151—153°. On boiling the quaternary iodide with 20% potassium hydroxide solution, a volatile oil was formed, presumably *6-bromopiperonylethylene*, but this rapidly polymerised to a plastic resin, insoluble in the ordinary solvents, which was not further investigated.

(b) *N*-Methyl-β-piperonylethylamine is dissolved in 7—10 parts of dilute hydrochloric acid, treated with the theoretical quantity of bromine diluted with a little acetic acid, and the product precipitated as hydriodide by the addition of a strong solution of potassium iodide.

Methylbromopiperonylethylamine is a colourless oil, readily soluble in benzene. The *hydrochloride* crystallises from alcohol–ether in small, stout needles, m. p. 162—164°, which give a claret-coloured solution in sulphuric acid, turned brown by potassium nitrate. The *hydriodide* forms small, white prisms, m. p. 175°, which dissolve readily in water or alcohol (Found : C, 31·5 ; H, 3·6. $C_{10}H_{12}O_2NBr,HI$ requires C, 31·1 ; H, 3·4%). The *benzoyl* derivative, obtained in the usual manner, crystallises from dilute methyl alcohol in clusters of colourless needles, m. p. 98—100° (Found : C, 56·4 ; H, 4·6. $C_{17}H_{16}O_3NBr$ requires C, 56·4 ; H, 4·4%).

N-*Methyl*-N-6′-*bromo*-β-*piperonylethyl*-6-*aminomethylhomopiperonylonitrile* (VIII).—The preparation is similar to that of the halogen-free compound (VII). As the hydrochloride is very sparingly soluble, it is best to evaporate the benzene, dissolve the residue in acetic acid, and pour the solution into hot, very dilute hydrochloric acid (100 c.c.). The mixture is treated with charcoal, and concentrated hydrochloric acid added; the hydrochloride then crystallises, on cooling, in colourless needles, m. p. 205° (Found : C, 51·2; H, 4·3. $C_{20}H_{19}O_4N_2Br,HCl$ requires C, 51·3; H, 4·3%. 0·1154 gave 0·0818 silver halides; theory demands 0·0818). It is sparingly soluble in water or alcohol and gives an emerald-green solution in concentrated sulphuric acid. The *nitrate* separates from dilute nitric acid, in which it is very difficultly soluble, as a microcrystalline powder which decomposes with effervescence at about 160° (Found : Br, 16·2. $C_{20}H_{19}O_4N_2Br,HNO_3$ requires Br, 16·2%).

Repeated attempts were made to bring about an internal Grignard reaction with this substance, but it could not be induced to react with magnesium under any conditions, and the bromine atom was not removed even by prolonged boiling in ligroin with " molecular " potassium.

6-*Methoxymethylhomopiperonylic Acid*.—(a) The lactone (3 g.) is boiled with chloroform (12 c.c.) and phosphorus trichloride (6 c.c.) for 5 hours, and the mixture is poured into excess of methyl alcohol and warmed on the steam-bath for 2 hours. After dilution with water, the *ester* (X) is extracted with chloroform and distilled in a vacuum; the greater part passes over at 199°/21 mm. as a colourless oil which solidifies in a freezing mixture. It crystallises from dilute methyl alcohol in white needles, m. p. 41—43° (Found : C, 60·2; H, 5·9. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%). The free *acid*, obtained by hydrolysis with methyl-alcoholic potassium hydroxide, forms colourless needles from benzene–light petroleum, m. p. 93—95°. The *silver* salt is sparingly soluble in hot water (Found: Ag, 32·5. $C_{11}H_{11}O_5Ag$ requires Ag, 32·6%). When the acid is heated with dilute hydrochloric acid (15%) for an hour on the steam-bath, a pink solution is produced which deposits the lactone (III) in an impure condition on cooling.

For purposes of comparison, homopiperonyl methyl ether was mixed with concentrated hydrochloric acid and enough acetic acid to give a homogeneous solution and heated on the steam-bath; crystals soon began to separate, and the ether was finally completely converted into 2 : 3 : 6 : 7-bismethylenedioxydihydroanthracene (XII), which was identified by its insolubility and high m. p., and its conversion, by treatment with nitric acid, into 6 : 6′-dinitro-3 : 4 : 3′ : 4′-bismethylenedioxydiphenylmethane (Ewins, *loc. cit.*; G. M. Robinson, *loc. cit.*), which did not depress the m. p. of an authentic specimen. Both samples of the dinitro-compound crystallised from acetic acid in yellow needles, and not in prisms, as described by Ewins, but gave the correct m. p. (217°).

(b) The methoxy-acid is also formed, along with much of the lactone (III), when bromomethylhomopiperonylic acid (XIII; *vide infra*) is boiled for 2 hours with excess of methyl alcohol, and any ester formed hydrolysed by means of potassium hydroxide.

6-*Bromomethylhomopiperonylic Acid* (XIII).—The lactone (III) is dissolved in a little hot acetic acid, and excess of a strong solution of hydrogen bromide in the same solvent added. After some hours, the white needles that have separated are collected, washed, and recrystallised from benzene. The acid is moderately easily soluble in warm acetic acid, less soluble in benzene or ether, melts at 146—149°, and decomposes at about 180° with evolution of hydrogen bromide (Found: Br, 29·7. $C_{10}H_9O_4Br$ requires Br, 29·3%). On treatment with sodium bicarbonate solution, it is reconverted into the lactone without dissolving completely. Attempts were made to condense the substance with β-piperonylethylamine or its *N*-methyl derivative, but under all conditions tried, even in presence of acetic acid, the lactone (III) was produced: with quinoline, on the other hand, a quaternary salt appeared to be formed, but this was not further investigated. The *methyl* ester is obtained by adding a solution of the acid in warm benzene to excess of diazomethane in well-cooled ether. After several hours, the solvents are evaporated and the residue is extracted several times with light petroleum. The ester separates from the concentrated extract, cooled in ice, and is recrystallised from benzene–light petroleum. It forms hard prisms, m. p. 68—70° with previous softening at about 64°, which are readily soluble in benzene, but sparingly soluble in light petroleum

(Found: Br, 28·1. $C_{11}H_{11}O_4Br$ requires Br, 27·9%). Both bromomethylhomopiperonylic acid and its ester very slowly turn pink on keeping.

N-*Methyl*-N-β-*piperonylethyl*-6-*aminomethylhomopiperonylic Acid* (XIV).—Methyl bromomethylhomopiperonylate (1 mol.), dissolved in benzene, is gradually added to a benzene solution of methyl-β-piperonylethylamine (2 mols.); heat is evolved and a solid rapidly separates. After the benzene has been evaporated, the ester group is hydrolysed by boiling for 1 hour with methyl-alcoholic potassium hydroxide, the liquid diluted, and the excess of methylpiperonylethylamine extracted with benzene. The aqueous layer is acidified, rendered alkaline with ammonia, concentrated, and a solution of oxalic acid added. On standing, the *oxalate* separates and is recrystallised from alcohol–ether and dried at 110°, forming warty aggregates of minute prisms, softening at 173° and melting with effervescence at 178° [Found: C, 60·8; H, 5·6. $(C_{20}H_{21}O_6N)_2,C_2H_2O_4$ requires C, 60·6; H, 5·3%]. Considerable difficulty was experienced in obtaining the free amino-acid in a crystalline condition. The oxalate is dissolved in alcohol, treated with alcoholic ammonia, the ammonium oxalate removed by filtration, and the residue evaporated to dryness and dried in a vacuum. A hard glassy mass remains which slowly crystallises on warming on the steam-bath. In this condition, the substance melts at 136—140°, and is readily soluble in methyl or ethyl alcohol, moderately soluble in chloroform or hot water, and almost insoluble in ether or benzene; it dissolves readily in ammonia, and gives a violet solution in concentrated sulphuric acid. From most of the solvents tried, the amino-acid separates as a gum, but it forms a microcrystalline powder, from chloroform–ether, which contains chloroform of crystallisation (carbylamine reaction), not removed in a steam-oven, and melts to a yellow froth at about 100°. In view of the small quantity available and the intractability of the substance it was not purified for analysis. By the action of thionyl chloride, it was converted into the acid chloride (not isolated), and the latter treated in nitrobenzene solution with aluminium chloride with a view to obtain the compound (II). Considerable decomposition took place, and no pure substance could be isolated in several experiments.

The author's thanks are due to the Ramsay Memorial Trustees for a Fellowship, and to Professor W. H. Perkin for suggesting this investigation and for his kindly interest in its progress.

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[*Received, November 24th,* 1926.]

XXX.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXI. The Resolution of* m-*Carboxyphenylmethylsulphine-*p-*toluenesulphonylimine.*

By SYDNEY GEORGE CLARKE, JOSEPH KENYON, and HENRY PHILLIPS.

RAPER discovered that the condensation of chloramine-T with dialkyl sulphides gave rise to compounds of a new type containing a quadrivalent sulphur atom linked to nitrogen. Such compounds were named sulphilimines by Mann and Pope (J., 1922, **121**, 1052), who expressed by the general formula $C_6H_4Me\cdot SO_2\cdot N{:}SXY$ the constitution of those sulphilimines arising by the use of chloramine-T. These authors (J., 1924, **125**, 911) also pointed out that "the sulphilimines might be expected to exist in enantiomorphously related forms owing to the operation of a trihedral disposition of the three valency directions of the doubly-linked nitrogen atom." It would appear from this statement that they considered that, in a sulphilimine of the above type, the *p*-toluenesulphonyl group was not in the same plane as the groups X and Y, a space arrangement which need not necessarily be similar (as Mann and Pope suggested it should be) to that existing in *cyclo*hexylene dithiocarbonate 2-pyridylhydrazone, which was resolved by Mills and Schindler (J., 1923, **123**, 312). This is true even if the $>S{:}N-$ group of the sulphilimine can produce a similar space arrangement as the $>C{:}N-$ group of the hydrazone. The problem involved was also considered by Mann and Pope to have a bearing on the question whether the four valencies of quadrivalent sulphur are identical or whether one is co-ordinated as was indicated by Werner ("Lehrbuch der Stereochemie," 1904, p. 316).

Mann and Pope prepared and examined *d*- and *l*-camphorylidenemethylethylsulphine-*p*-toluenesulphonylimine

$$(C_{10}H_{14}O{:}CH\cdot SEt{:}N\cdot SO_2\cdot C_6H_4Me)$$

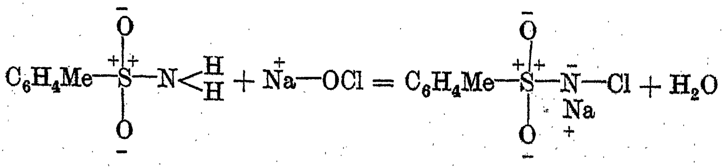
and stated that neither of these compounds furnished any indication of stereoisomerism of the type *d*-C,*d*-S and *d*-C,*l*-S and that therefore they proposed to investigate other methods for realising this type of isomerism.

In this communication, however, it is suggested that the sulphilimines contain the group $>\overset{+}{S}-\overset{-}{N}-$. Any question as to the disposition in space of the three valency directions of the nitrogen atom, which is now linked by two covalencies and one electrovalency, must therefore be left in abeyance. It is nevertheless suggested that sulphilimines of the type $C_6H_4Me{\cdot}SO_2{\cdot}\overset{-}{N}{\cdot}\overset{+}{S}XY$ should be capable of existing in enantiomorphously-related forms, since the quadrivalent sulphur atoms which they contain are in a state of combination analogous to that of the quadrivalent sulphur atoms of the esters of *p*-toluenesulphinic acid and of mixed sulphoxides the optically active forms of which have been described (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, J., 1926, 2079). In other words, the positively charged sulphur atom of the sulphilimine molecule can be considered to occupy the apex of a tetrahedron at the other three corners of which lie the groups X and Y and the *p*-toluenesulphonamido-group the nitrogen atom of which bears a negative charge.

To support these suggestions, it is necessary to review the constitution of chloramine-T and its reactions with thio-ethers in the light of the newer electronic theories of valency and the investigations to which those theories have given rise.

The Constitution of Chloramine-T.

Sugden, Reed, and Wilkins (J., 1925, **127**, 1525) have shown, by measurements of the molecular parachors of compounds containing a sexavalent sulphur atom linked to two oxygen atoms (*e.g.*, ethyl ethanesulphonate), that in such compounds the sulphur and oxygen atoms are linked by semipolar double bonds as had been suggested by Lowry (*Trans. Faraday Soc.*, 1923, **18**, 285). Hence the constitution of *p*-toluenesulphonamide, the parent substance of chloramine-T, is doubtless more accurately represented by the formula given in the equation below than by the structural formula by which it is usually indicated. The reaction which occurs when *p*-toluenesulphonamide is converted into chloramine-T by the action of sodium hypochlorite (Dakin, Cohen, Daufresne, and Kenyon, *Proc. Roy. Soc.*, 1916, *B*, **89**, 236) can then be represented by the following equation:

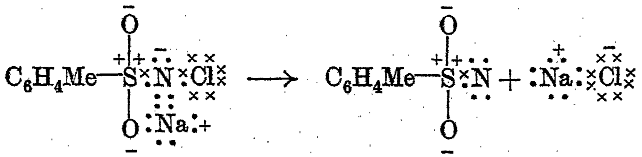


$$C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{++}{S}}}-N{<}^{H}_{H} + \overset{+}{Na}-OCl = C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{++}{S}}}-\underset{\underset{+}{Na}}{\overset{-}{N}}-Cl + H_2O$$

Thus it is suggested that the valencies of the tervalent nitrogen atom which chloramine-T contains are made up of two covalencies and one electrovalency. If, therefore, the sodium ion is considered to be closely attracted to the nitrogen atom, then this atom possesses the same type of tricovalency as that of the nitrogen atom of sodium phthalimide. It should be noticed, however, that the sodium ion can become attracted to either of the negatively charged sulphoxy-oxygen atoms in the molecule without causing any change in the mode of linking of the nitrogen atom. Hence it would appear that the formulation of chloramine-T as a derivative of *iso*chloramine with the constitution $C_6H_4Me{\cdot}SO(ONa){:}NCl$ (compare Chattaway, J., 1905, **87**, 146, 153; Dakin, Cohen, Daufresne, and Kenyon, *loc. cit.*; Mann and Pope, *loc. cit.*) is not only unnecessary but misleading, since it requires that the sexavalent sulphur atom should be surrounded by twelve valency electrons instead of the normal octet the presence of which around the sulphur atom in such compounds agrees with the experimental results of Sugden, Reed, and Wilkins (*loc. cit.*).

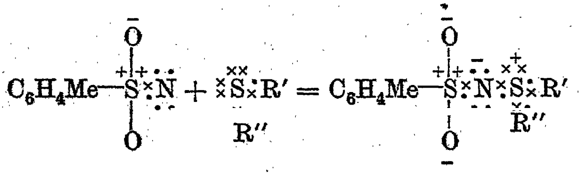
The Condensation of Chloramine-T with Thio-ethers.

The constitutional formula of a sulphilimine is more easily deduced if the condensation of the chloramine-T with the thio-ether is assumed to occur in two stages. Under the experimental conditions employed, during the first stage of the reaction the chloramine-T can be considered to decompose into sodium chloride and an active radical:



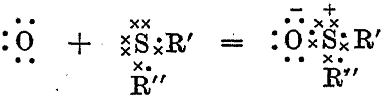
$$C_6H_4Me-\underset{\underset{\bar{O}\,:Na:^{+}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\bar{\cdot\cdot}\;\times\times}{\times N{:}\times Cl\times} \longrightarrow C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\cdot\cdot}{\times N} + \overset{+}{:Na:}\overset{-}{\times Cl\times}$$

In the above formulæ the electrons represented by crosses in the valency octet of the nitrogen atom are contributed to that octet by the sulphur and chlorine atoms to which the nitrogen atom is united by covalencies. When chloramine-T decomposes as indicated above, it loses the chlorine atom as *an ion* and hence the active radical produced contains a nitrogen atom surrounded by a sextet of valency electrons. It can then be assumed that during the second stage of the condensation this nitrogen atom completes its octet at the expense of one of the two lone pairs of electrons present in the valency shell of the sulphur atom which the thio-ether contains.



$$C_6H_4Me-\underset{\underset{O}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\cdot\cdot}{\times N} + \underset{R''}{\overset{\times\times}{\times S\times}}R' = C_6H_4Me-\underset{\underset{\bar{O}}{|}}{\overset{\overset{\bar{O}}{|}}{\overset{+\,+}{S}}}\overset{\bar{\cdot\cdot}}{\times N\times}\underset{R''}{\overset{+}{S}}\times R'$$

These electronic formulæ reveal two points of interest. First, the nitrogen and sulphur atoms cannot become united by a true double bond (non-polar double bond), since such a linking would create a surplus of electrons (10 instead of 8) in the valency shells of both atoms. Secondly, the sulphur atom contributes both electrons to form the covalency by which it is subsequently united to the nitrogen atom, and after the union one of these electrons functions as though it had been contributed originally by the nitrogen atom. Hence the nitrogen atom acquires a negative charge (having gained an electron or, alternatively, gained a half share of two electrons), whilst the sulphur atom (having lost an electron, or, alternatively, lost a half share in two electrons) acquires a positive charge. The nitrogen and sulphur atoms thus become united by a semipolar double bond. When viewed from this standpoint, the formation of the sulphilimine becomes strictly analogous to the oxidation of a sulphide to a sulphoxide.



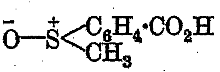
$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} + {}^{\times}_{\times}\overset{\times\times}{\underset{\underset{R''}{\times\cdot}}{S}}{}^{\times}_{\times}R' = :\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}{}^{\times}_{\times}\overset{\times\times\,+}{\underset{\underset{R''}{\times\cdot}}{S}}{}^{\times}_{\times}R'$$

In this instance, the neutral oxygen atom with a sextet of valency electrons completes its octet, as did the nitrogen atom of the *p*-toluenesulphonamido-radical, at the expense of the valency electrons of the sulphur atom.

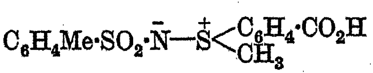
Resolution of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine.*

Since *dl*-*m*-carboxyphenyl methyl sulphoxide (I) was successfully resolved into its optically active forms by Harrison, Kenyon, and

(I.)



$$\overset{-}{O}-\overset{+}{S}<\begin{matrix}C_6H_4\cdot CO_2H\\ CH_3\end{matrix}$$



$$C_6H_4Me\cdot SO_2\cdot\overset{-}{N}-\overset{+}{S}<\begin{matrix}C_6H_4\cdot CO_2H\\ CH_3\end{matrix}$$

(II.)

Phillips (*loc. cit.*), there appeared to be no reason, if the above arguments are valid, why the corresponding sulphilimine (II) should not also be capable of existing in enantiomorphously related forms. dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* was therefore prepared and examined. It was readily obtained by the condensation of chloramine-T with *m*-carboxyphenyl methyl sulphide. Its *brucine* salt, on recrystallisation from acetone, changed rapidly in rotatory power, and when optically pure the *l*-B, *l*-A salt had $[\alpha]_{5461}$ −144° in ethyl-alcoholic solution. On decomposition of this salt with dilute hydrochloric acid the l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* was obtained with $[\alpha]_{5461}$ −338°, $[\alpha]_{4359}$ −627° in ethyl-alcoholic solution. The more soluble brucine salt was recovered from the mother-liquors from the crystallisations of the *l*-B, *l*-A salt, and on decomposition gave a sulphilimine with $[\alpha]_{5461}$ +145°. This sulphilimine was combined with cinchonidine and the *cinchonidine* salt obtained was repeatedly crystallised from ethyl alcohol until its rotatory power was constant. It then had $[\alpha]_{5461}$ +48·3° in chloroform and on decomposition gave d-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* with $[\alpha]_{5461}$ +337°, $[\alpha]_{4359}$ +627° in ethyl-alcoholic solution. The satisfactory agreement between the specific rotatory powers of the two enantiomorphs indicates that both were obtained optically pure. The specific rotatory powers of the optically pure sulphilimine in various solvents are in Table I.

TABLE I.

Specific Rotatory Powers of l-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine in Solvents.*

c = g. of *l*-sulphilimine in 100 c.c. of solution. $l = 2$. $a_\lambda = 0{\cdot}02c[\alpha]_\lambda$.

Solvents.	c.	λ_{6708}.	λ_{5893}.	λ_{5780}.	λ_{5461}.	λ_{4359}.
Ethyl alcohol	3·0000	209°	276°	293°	338°	627°
Pyridine	3·0000	190	255	265	308	583
Chloroform	0·2505	216	272	288	332	609
Ethyl acetate	0·4146	190	260	267	306	570
Glacial acetic acid ...	2·0000	190	253	266	306	569

This table shows that the specific rotatory power of the optically active sulphilimine is but slightly influenced by solvents. Under the experimental conditions employed, the sulphilimine exhibits complex rotatory dispersion (except possibly when dissolved in ethyl acetate), since curves are obtained when $1/\alpha$ for this compound is plotted against λ^2. Unlike the optically active sulphoxides previously described (Harrison, Kenyon, and Phillips, *loc. cit.*), which differed considerably in physical properties from their racemic modifications, the optically active sulphilimine now described is closely similar to the optically inactive compound. The specific rotatory power of the sulphilimine in solvents remains unchanged on standing, and in this respect it resembles the optically active sulphoxides (*loc. cit.*) rather than the esters of *p*-toluenesulphinic acid (Phillips, *loc. cit.*, p. 2573), which exhibit marked mutarotation in solution.

dl-*m*-Carboxyphenylmethylsulphine-*p*-toluenesulphonylimine was converted by the action of dilute hydrochloric acid into a mixture of *p*-toluenesulphonamide, *m*-carboxyphenyl methyl sulphide and sulphoxide, whilst the sulphonamide and *m*-carboxyphenylmethylsulphone were the sole products of the action of hydrogen peroxide. Further experiments are under consideration with the object of converting the sulphilimine into an unsymmetrical compound containing sexavalent sulphur.

EXPERIMENTAL.

dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*.—To a solution of *m*-methylthiolbenzoic acid (100 g.) in warm alcohol (500 c.c.) made just alkaline by the addition of 3*N*-sodium hydroxide, chloramine-T (190 g.; 1·1 mols.) in warm water (550 c.c.) was added, and the mixture heated on a steam-bath for 2 hours. Dilute hydrochloric acid was added to the resulting solution after cooling and dl-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* then separated, m. p. 160—164°. Yield 150 g. (75%). By recrystallisation from aqueous ethyl alcohol it was obtained as small needles, m. p. 173—175° (Found: C, 53·6; H, 4·5; N, 4·2. $C_{15}H_{15}O_4NS_2$ requires C, 53·4; H, 4·5; N, 4·2%. 0·3370 required 0·0404 of sodium hydroxide; theory requires 0·0400).

Resolution of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine*.—(a) *By means of brucine.* To *dl*-*m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (105 g.) in acetone (500 c.c.), brucine (124 g.) was added, and the mixture was warmed until solution was complete. After cooling, the brucine salt (m. p. 95—105°) which crystallised was removed and recrystallised from four successive quantities (about 1000 c.c. in each case) of acetone until constancy of rotatory power was reached.

l-*Brucine* l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* had m. p. 123—125°, $[\alpha]_{5461}$ −144°, $[\alpha]_{4359}$ −279° in ethyl alcohol ($l = 2$; $c = 2·500$).

The optically pure salt, dissolved in warm ethyl alcohol, was added to dilute hydrochloric acid. After 48 hours, the l-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* had separated completely. It crystallised from aqueous ethyl alcohol in prismatic needles, m. p. 172—173°. Its specific rotatory power in various solvents is recorded in Table I.

(b) *By means of cinchonidine.* The acetone mother-liquor from the first crystallisation of the brucine salt described above was added to dilute hydrochloric acid. The *d* + *dl*-*m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (18·5 g.; with $[\alpha]_{5461}$ +145°) which was precipitated was dissolved in ethyl alcohol (70 c.c.) and to the warm solution cinchonidine was added (16·1 g.). After standing over-night, the cinchonidine salt, m. p. 193—194°, was removed by filtration and repeatedly crystallised from the minimum of ethyl alcohol (about 200 c.c.) until its rotatory power remained unchanged. The l-*cinchonidine* d-m-*carboxyphenylmethylsulphine*-p-*toluenesulphonylimine* thus obtained had m. p. 204°, and $[\alpha]_{6708}^{17·5°}$ +29·42°, $[\alpha]_{5893}^{17·5°}$ +38·47°, $[\alpha]_{5780}^{17·5°}$ +46·76°, $[\alpha]_{5461}^{17·5°}$ + 48·27°, $[\alpha]_{4358}^{17·5°}$ + 102·6°, in chloroform solution ($c = 1·326$, $l = 2·0$). On decomposition, as previously described, it gave d-*carboxyphenyl-*

methylsulphine-p-*toluenesulphonylimine*, m. p. 172—173°, $[\alpha]_{5461}$ $+337°$, $[\alpha]_{4359}$ $+627°$ in ethyl alcohol ($c = 2{\cdot}59$, $l = 1{\cdot}0$).

The Interaction of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine and Hydrochloric Acid*.—A clear deep red solution was obtained by heating the *dl*-sulphilimine (6·74 g.) with concentrated hydrochloric acid (18 c.c.) on a steam-bath for 5 minutes. From the solution, neutralised by means of sodium carbonate, *p*-toluenesulphonamide (1·62 g.), m. p. 137°, was precipitated, whilst the products which remained dissolved consisted of two acids which were obtained after acidification of the concentrated solution, and were separated by fractional crystallisation from aqueous ethyl alcohol into *m*-carboxyphenyl methyl sulphoxide (1·4 g.), m. p. 171°, and *m*-methylthiolbenzoic acid (1·45 g.), m. p. 127—128°. The overall yield of hydrolytic products was therefore 66%.

The Interaction of dl-m-*Carboxyphenylmethylsulphine*-p-*toluenesulphonylimine and Hydrogen Peroxide*.—A mixture of the sulphilimine (2 g.) and perhydrol (20 c.c.) was heated on a steam-bath with occasional shaking; a clear solution resulted after 15 minutes. The crystalline material (1·6 g.), m. p. 130—180°, which separated on cooling, was crystallised from a small bulk of ethyl alcohol, glistening leaflets (0·7 g.) of *m*-carboxyphenylmethylsulphone (m. p. 229—230° either alone or mixed with an authentic specimen) being obtained. After dilution, the filtrate yielded a second crop of crystals (0·9 g.) which proved to be *p*-toluenesulphonamide, m. p. 135—136°. The original hydrogen peroxide filtrate was evaporated to small bulk; a further quantity (0·29 g.) of *m*-carboxyphenylmethylsulphone was then obtained.

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[*Received, December 7th,* 1926.]

XXXI.—*Studies in the Penthian* Series. Part I. The Action of Sodium Ethoxide on Ethyl β-Thiodipropionate.*

By GEORGE MACDONALD BENNETT and LESLIE VIVIAN DONALD SCORAH.

THE researches of V. Meyer and his students led to the isolation of 3-methylpenthiophen (3-methyl-$\Delta^{2:5}$-penthiadiene) in very poor yield from the products of distillation of α-methylglutaric acid with phosphorus trisulphide (Krekeler, *Ber.*, 1886, **19**, 3266), but very little has since been added to our knowledge of the chemistry of compounds containing this ring system. Penthian itself (v. Braun and Trümpler, *Ber.*, 1910, **43**, 547; Clarke, J., 1912, **101**, 1805) and its 2-methyl derivative (Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 928) have been prepared by the closure of the ring by the action of sodium sulphide on the αε-dihalogenated paraffin, whilst Apitzsch (*Ber.*, 1904, **37**, 1599; 1905, **38**, 2888; 1908, **41**, 4028; 1909, **42**, 2940) has shown that the products of condensation of carbon disulphide and ketones are derived from penthiadien-4-one.

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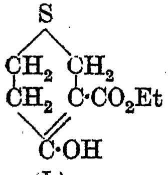
* In order to simplify the nomenclature of this group, we propose, after consultation with the Editor, to name the parent substance (tetrahydropenthiophen or pentamethylene sulphide) *penthian*.

Simple substituted derivatives of penthian have not hitherto been prepared by smooth ring-closure from open-chain compounds. V. Meyer suggested (*Ber.*, 1886, **19**, 3260) the application of the malonic ester method to ββ′-dichlorodiethyl sulphide for this purpose, but this reaction has recently been shown by Davies (J., 1920, **117**, 297) to yield under various conditions, not the desired penthiandicarboxylic ester, but solely the open-chain tetracarboxylic ester, $S[CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2]_2$. We have now subjected ethyl β-thiodipropionate, $S(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, to the Dieckmann reaction: the reaction proceeds readily in presence of sodium ethoxide or sodamide to yield the oily enolic ester (I), *ethyl* Δ^3*-penthien-4-ol-3-carboxylate*, which gives an intense purple coloration with ferric chloride. This ester, on keeping, ultimately deposits long needles of the ketonic ester (II), *ethyl penthian-4-one-3-carboxylate*, which gives a delayed reaction with ferric chloride and dissolves only slowly in aqueous solutions of sodium hydroxide.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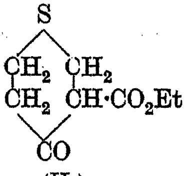
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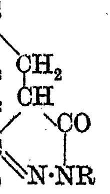
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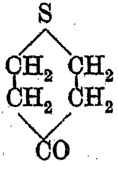
(IV.)

That this ester has a β-ketonic structure is confirmed by its condensation with hydrazines to yield pyrazolones of the general formula (III), and by its hydrolysis by cold dilute alkali or hot dilute acid to give a crystalline ketone, *penthian-4-one* (IV), readily volatile in steam. Penthianone furnishes, not only the usual derivatives of a cyclic ketone, such as the *oxime*, the *semicarbazone*, the *dinitrophenylhydrazone* and the *dibenzylidene* derivative, but also others due to the reactivity of the sulphur atom, namely, a crystalline *sulphonium methiodide* and a *platinic chloride* compound of the composition $2C_5H_8OS,PtCl_4$.

The yield of cyclic ester (43%) obtained in this investigation was consistently lower than that (60%) in the analogous reaction with ethyl pimelate carried out by Dieckmann (*Annalen*, 1901, **317**, 93). This raises the question whether the substitution of a sulphur atom for a methylene group in a chain diminishes the tendency to ring closure.

As far as we are aware, these experiments constitute the first instance of the closure of a simple heterocyclic ring by means of the Dieckmann reaction. The method should be applicable in a similar manner to analogous substances where sulphur is replaced by oxygen, nitrogen, or other element.

EXPERIMENTAL.

Preparation of β-*Thiodipropionic Acid and its Derivatives.*—The preparation described by Loven (*Ber.*, 1896, **29**, 1136) was modified as follows: To a solution of potassium hydroxide (23·5 g.) and sodium sulphide (72 g. of $Na_2S,9H_2O$) in water (190 c.c.), β-iodopropionic acid (100 g.) was added and the mixture was boiled for 15 minutes, cooled to − 10°, and acidified with concentrated hydrochloric acid (50 c.c.). The acid, filtered off after a few hours and washed with a little water, was practically pure (yield 70%). It may be recrystallised from hot water or xylene. It was more economically obtained and in slightly better yield by substituting β-bromopropionic acid (77 g.) for the iodo-acid in the above preparation, and boiling the mixture for 1 hour. A further addition to the yield is obtained by extracting the mother-liquor with ether.

Thiodipropiondiamide, prepared by the action of concentrated aqueous ammonia on the ester (see below) or on the acid chloride obtained from thiodipropionic acid by the action of thionyl chloride, crystallised from ethyl alcohol in colourless plates, m. p. 177—178·5° (Found: N, 15·6; S, 18·2. $C_6H_{12}O_2N_2S$ requires N, 15·9; S, 18·2%).* *Thiodipropiondianilide*, prepared from the acid and boiling aniline in the usual manner, separated from toluene in colourless scales, m. p. 163·5° (Found: N, 8·5; S, 9·8. $C_{18}H_{20}O_2N_2S$ requires N, 8·5; S, 9·8%).

Ethyl thiodipropionate was obtained as a pale straw-coloured oil, b. p. 174°/15 mm. (yield 70% by the Fischer and Speier method; 90% by the continuous process as in "Organic Syntheses," **1**, 68). It has a strong, unpleasant odour, and does not solidify at − 20° (Found: S, 13·8, 13·6; equiv. by saponification, 117·4. $C_{10}H_{18}O_4S$ requires S, 13·7%; equiv., 117·1). The following constants were determined: $d_{4^\circ}^{20^\circ}$ (vac.) 1·1034, $n_\alpha^{20^\circ}$ 1·46938, $n_\beta^{20^\circ}$ 1·47911, whence $[R_L]_\alpha$ 59·17 (calc., 59·30) and $[R_L]_\beta$ 60·20 (calc., 60·29).

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* Determinations of sulphur were made by the method of Leonard (*J. Amer. Chem. Soc.*, 1923, **45**, 255).

Ethyl Penthian-4-one-3-carboxylate.—Preliminary experiments showed that ethyl thiodipropionate, subjected to the action of sodium metal in boiling toluene (Bouveault, *Bull. Soc. chim.*, 1899, **21**, 1019), suffered profound decomposition with production of much sodium sulphide. It was found best to use sodium ethoxide at a low temperature in the following manner: To sodium ethoxide, made from Brühl sodium (8 g.) in a flask fitted with a stirrer and a reflux condenser, a solution of ethyl thiodipropionate (40 g.) in dry ether (150 c.c.) was carefully added. The mixture, cooled in a freezing mixture, was stirred for 6 hours, allowed to rise to the ordinary temperature over-night, and then poured into a mixture of ice and acetic acid (22 g.). The lower aqueous layer was removed and extracted twice with ether and the extracts were added to the original ethereal layer. The ethereal solution was then shaken seven times with diminishing amounts of 5% potassium hydroxide solution (530 c.c. in all), the alkaline solution in each case being immediately run into a mixture of ice and acetic acid. The oil thus precipitated was collected in carbon tetrachloride and the extract was shaken twice with *N*/2-sodium carbonate (100 c.c.) to remove the acid ester which was present, and distilled. *Ethyl* Δ^3-*penthien-4-ol-3-carboxylate* (I) (14 g.; 43% yield) was thus obtained as an almost colourless oil of characteristic odour, b. p. 150—151°/16 mm. (Found: C, 50·7; H, 6·5; S, 17·3. $C_8H_{12}O_3S$ requires C, 51·0; H, 6·4; S, 17·0%). This ester gives an immediate purple coloration with alcoholic ferric chloride and dissolves at once in aqueous sodium hydroxide. The residual ethereal solution in the above preparation yielded ethyl thiodipropionate (4 g.) on distillation. A slightly higher yield of the cyclic ester was obtained when sodamide (2 mols.) was used in place of sodium ethoxide. The following constants were determined with a freshly-prepared specimen of the ester which had been twice redistilled, the initial and the final fractions being rejected: $d_{4^\circ}^{20^\circ}$ (vac.) 1·2011, $n_{\alpha}^{20^\circ}$ 1·51574, $n_{\beta}^{20^\circ}$ 1·52938, whence $[R_L]_\alpha$ 47·29 (calc., 47·35) and $[R_L]_\beta$ 48·34 (calc., 48·33).*

When this enolic ester had been kept for about a week, it began to deposit crystals of its ketonic tautomeric form, *ethyl penthian-*

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* The values in brackets have been calculated using the constants for sulphides found by Price and Twiss (J., 1912, **101**, 1259). No allowance was made for ring-closure, this being justified by the value for penthian itself found by Clarke (*ibid.*, 1800): $[R_L]_\alpha$ 30·61 (calc., 30·84). The values calculated for the ketonic form of the ester would have been 46·21 and 47·20, respectively. It must be admitted that the agreement obtained above may be in part fortuitous, since an exaltation due to conjugation is to be expected in an enolic form: moreover, it is probable that the enolic ester examined already contained some of the ketonic form.

4-*one*-3-*carboxylate* (II), which was dried on porous earthenware and obtained as colourless needles having a high double refraction and an oblique extinction, being probably monoclinic; m. p. 59° (Found: C, 51·05; H, 6·0. $C_8H_{12}O_3S$ requires C, 51·0; H, 6·4%).

This substance differs from the enolic ester in that it dissolves only slowly in aqueous sodium hydroxide and gives no immediate coloration with ferric chloride, the purple colour appearing and increasing in intensity for several minutes. The coloration is not destroyed by the addition of dilute acetic acid. Concentrated aqueous barium hydroxide acts on either of the esters to produce a sparingly soluble, pale yellow *barium* salt. No crystalline copper salt could be obtained.

Pyrazolone Derivatives (III).—The freshly-distilled enolic ester (2 g.) condensed with phenylhydrazine (1·19 g.) on being heated with it and two drops of acetic acid at 100° for 2 hours. The *phenylpyrazolone* crystallised from methyl alcohol in cream-coloured needles, m. p. 219° (Found: N, 12·1. $C_{12}H_{12}ON_2S$ requires N, 12·1%). The reactions between the ester and *p*-bromo- and *p*-nitrophenylhydrazine were carried out in ethyl-alcoholic solution, equimolecular quantities being heated at its boiling point in presence of a few drops of acetic acid for 4 hours. The p-*bromophenylpyrazolone* crystallises from glacial acetic acid in almost colourless plates, m. p. 221·5° (Found: N, 8·7; Br, 25·8. $C_{12}H_{11}ON_2BrS$ requires N, 9·0; Br, 25·7%). The p-*nitrophenylpyrazolone* forms buff-coloured plates from alcohol; m. p. 210·5° (Found: N, 15·1. $C_{12}H_{11}O_3N_3S$ requires N, 15·2%).

Hydrolysis of the Cyclic Ester to yield Penthian-4-*one*.—The cyclic ester (5 g.) was kept for 3 days at the ordinary temperature with 5% potassium hydroxide solution (60 c.c.), the mixture was then extracted with ether, and the ether evaporated. The residue (1·5 g.), which crystallised at once, was *penthian*-4-*one* (IV). This substance separates from petroleum (b. p. 40—60°) in tufts of colourless plates, m. p. 65—66° (Found: C, 51·7; H, 6·9. C_5H_8OS requires C, 51·7; H, 6·9%). The crystals are biaxial with a straight extinction, being probably monoclinic; an optic axis is visible in convergent polarised light and the double refraction is exceptionally high. The substance is appreciably volatile at the ordinary temperature and readily so in steam. It has a strong, characteristic odour and is readily soluble in all the usual organic solvents, slightly less soluble in light petroleum, and moderately easily soluble in cold water.

Preliminary experiments had shown the hydrolysis of the cyclic ester by means of barium hydroxide solution to be very slow and incomplete, probably owing to the sparing solubility of the barium salt which was at once precipitated. On the other hand, acid hydrolysis was very effective; the ester (1·2 g.) was boiled with 10% sulphuric acid (10 c.c.) for 4 hours; the solution then deposited some of the ketone in a crystalline condition on cooling. Extraction with ether and crystallisation of the residue from light petroleum gave the pure ketone (0·64 g.; 85% yield).

Direct Preparation of Penthianone from Ethyl Thiodipropionate.—The ketone is most conveniently prepared by allowing ethyl thiodipropionate (40 g.) to react with sodium ethoxide (from 8 g. of sodium) as previously described, pouring the reaction mixture into water, removing the upper ethereal layer and extracting it three times with potassium hydroxide solution (5%: 300 c.c.), and keeping the combined alkaline aqueous solutions for 3 days; extraction with ether then yields the ketone (6·7 g.; 33% yield).

Derivatives of Penthianone.—The *oxime*, prepared in aqueous solution and isolated by extraction with ether, is readily soluble in most solvents. It crystallises from warm water, in which it is easily soluble, in colourless, flat needles, m. p. 84—85° (Found: N, 10·7. C_5H_9ONS requires N, 10·7%). The *semicarbazone*, prepared by means of semicarbazide acetate, was crystallised once from toluene, in which it is sparingly soluble, and once from ethyl acetate, in which it is readily soluble, as silvery plates, m. p. 151° (Found: N, 24·2. $C_6H_{11}ON_3S$ requires N, 24·3%). The 2 : 4-*dinitrophenylhydrazone* was precipitated at once on mixing the ketone and the hydrazine (1 mol.) in glacial acetic acid solution; it crystallised from this solvent, in which it is very sparingly soluble, in orange plates, m. p. 186° (Found: N, 18·9. $C_{11}H_{12}O_4N_4S$ requires N, 18·9%).

To a solution of the ketone (0·15 g.) and benzaldehyde (0·35 g.) in ethyl alcohol (2 c.c.), 25% potassium hydroxide solution (10 drops) was added. After a short time, the mixture became a paste of crystals of *dibenzylidenepenthianone*. The substance was crystallised once from ethyl alcohol and once from petroleum (b. p. 90—120°), from which it separated in yellow, compact tufts of crystals, m. p. 149—151° (Found: C, 77·8; H, 5·6. $C_{19}H_{16}OS$ requires C, 78·0; H, 5·5%).

The *dipiperonylidene* derivative, prepared in a precisely similar manner, crystallised from ethyl acetate in yellow tufts of pointed needles, m. p. 181°. It is more soluble in the common solvents than is the benzylidene derivative.

A *compound* with platinic chloride was obtained as a microcrystalline powder by mixing the components in dilute methylalcoholic solution, the precipitate appearing after the mixture had remained for a short time at the ordinary temperature. It was collected, washed with a little water, and dried in a desiccator. It is easily soluble in epichlorohydrin, from which it crystallises in small, yellow polyhedra which decompose on heating without melting (Found: Pt, 35·2. $C_{10}H_{16}O_2Cl_4S_2Pt$ requires Pt, 34·3%).

The ketone combined slowly with methyl iodide in cold benzene solution, but much more rapidly in the absence of a solvent, a solution of the ketone in an excess of methyl iodide depositing a mass of crystals in the course of a few days. The *penthianone-methylsulphonium iodide* thus obtained was insoluble in benzene, acetone or absolute ethyl alcohol, very soluble in water, and separated from 96% alcohol in pale yellow crystals, m. p. 112—113° (with effervescence due to dissociation) (Found: I, 48·9. $C_6H_{11}OIS$ requires I, 49·2%). An aqueous solution of this salt was digested with an excess of freshly-precipitated silver chloride and the resulting solution of the corresponding chloride was mixed with an excess of platinic chloride, but no chloroplatinate separated from solution even after long keeping. This chloroplatinate must therefore be unusually soluble in water.

Our thanks are due to the Chemical Society for a grant which has defrayed most of the expense of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, November 30th, 1926.*]

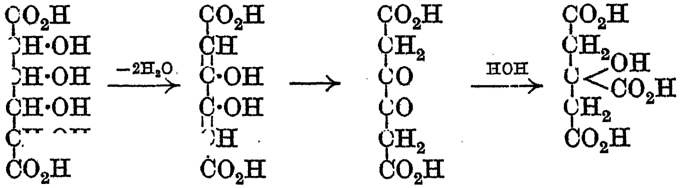
XXXII.—*The Mechanism of the Formation of Citric and Oxalic Acids from Sugars by* Aspergillus Niger. *Part I.*

By FREDERICK CHALLENGER, VIRA SUBRAMANIAM, and THOMAS KENNEDY WALKER.

THE production of citric and oxalic acids during the growth of *Aspergillus niger* and similar organisms on glucose or sucrose was first demonstrated by Wehmer (*Bot. Ztg.*, 1891, **49**, 233; *Bull. Soc. chim.*, 1893, **9**, 728; *Ber.*, 1924, **57**, 1659) and has formed the subject of various patent specifications (D.R.-PP. 72957, 91891). This transformation was further investigated by Currie (*J. Biol. Chem.*, 1917, **31**, 33) and by Butkewitsch (*Biochem. Z.*, 1923, **136**, 225; **142**, 195; 1924, **145**, 458).

Molliard (*Compt. rend.*, 1922, **174**, 881; 1924, **178**, 41, 161), Bernhauer (*Biochem. Z.*, 1924, **153**, 517; 1926, **172**, 296), and Butkewitsch (*ibid.*, 1924, **154**, 177) detected gluconic acid at an early stage of the fermentation, but were unable to convert this acid into citric acid under the conditions of their experiments. This has recently been accomplished by Wehmer (*Ber.*, 1925, **58**, 2616) and by Schreyer (*ibid.*, 2647). Gluconic acid appears to be the first step in the conversion of sugar into citric acid, although some difference of opinion has existed upon this point (Molliard, *loc. cit.*; Falck and Kapur, *Ber.*, 1924, **57**, 920).

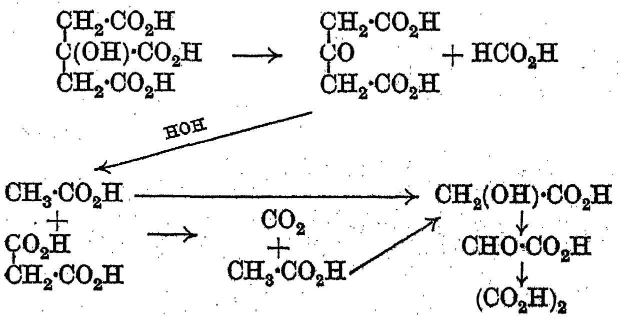
Franzen and Schmitt (*Ber.*, 1925, **58**, 222) have shown that $\beta\gamma$-diketoadipic acid (III) undergoes a "benzilic acid transformation" in presence of alkali-metal hydroxide, yielding citric acid (IV), and suggested that the biological formation of this acid proceeds in an analogous manner, the diketo-acid being supposed to arise from saccharic acid (I), although the production of this acid from sugar by mycological action had not been demonstrated:



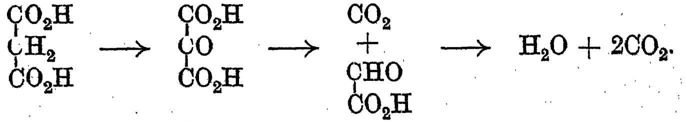
(I.) (II.) (III.) (IV.)

Two of the present authors have commenced a comprehensive investigation of the production of organic acids by *A. niger*, and the present communication describes results which have been obtained from a study of the conversion of citric into oxalic acid by the mould. This stage of the oxalic fermentation has received little attention from previous workers with the exception of Raistrick and Clark (*Biochem. J.*, 1919, **13**, 329), who examined the action of *A. niger* on various possible intermediate products.

In an endeavour to discover the mechanism of this process, a hypothesis was formulated which, from purely chemical considerations, might be regarded as a possible explanation. A search has been made in various cultures for some of the intermediate products thus suggested, and conversely the behaviour of these compounds to the mould has been studied. The tentative explanation of the decomposition of citric acid is represented by the scheme:



Raistrick and Clark (*loc. cit.*) found scarcely any oxalic acid when the mould was grown upon malonic, glyoxylic, or glycollic acid. The possibility of a conversion of malonic acid into carbon dioxide by way of mesoxalic and glyoxylic acids is not excluded :



$$\begin{array}{c}CO_2H\\ |\\ CH_2\\ |\\ CO_2H\end{array} \longrightarrow \begin{array}{c}CO_2H\\ |\\ CO\\ |\\ CO_2H\end{array} \longrightarrow \begin{array}{c}CO_2\\ +\\ CHO\\ |\\ CO_2H\end{array} \longrightarrow H_2O + 2CO_2.$$

The culture medium used throughout the present research was that of Molliard (*Compt. rend.*, 1919, **168**, 360), in which the amount of inorganic salts is the minimum. The sugar was entirely replaced by citric or other organic acid. The *Aspergillus* strain was kindly supplied by Professor Carl Neuberg, of Berlin-Dahlem, and the solutions were incubated at 30—32°.

In three separate experiments, the formation of glyoxylic acid was observed after 15, 17, and 18 days, respectively. This was first detected by the reddish-violet colour produced with hydrochloric acid and naphtharesorcinol (1 : 3-dihydroxynaphthalene, Neuberg, *Biochem. Z.*, 1910, **24**, 436) and afterwards as the aminoguanidine derivative (Döbner and Gärtner, *Annalen*, 1901, **315**, 8; **317**, 157). Glyoxylic acid was also obtained by the action of *A. niger* on solutions containing only malonic acid and the inorganic salts of the medium. It was characterised as before.

It does not necessarily follow, although it is very probable, that glyoxylic acid is a stage in the citric ⟶ oxalic change. The quantities of the aminoguanidine derivative so far obtained are too small to warrant definite conclusions on this point. They were, however, precipitated in very dilute solution. Dakin (*J. Biol. Chem.*, 1906, **1**, 271) states that glyoxylic acid is frequently detected in cultures of moulds and bacteria, but gives no details. He also found traces of this acid in sterilised media containing glycine or creatinine. The possibility that the aminoguanidine derivative might arise from traces of glyoxylic acid in the glacial acetic acid employed by us has been excluded by blank experiments and the use of pure acetic acid.

Cultures of the mould on citric acid were next examined for the presence of malonic acid, and this was detected in several experiments by addition of benzenediazonium chloride and sodium acetate, hydrogen formazyl, $CH(N_2Ph){:}N{\cdot}NHPh$ (von Pechmann, *Ber.*, 1892, **25**, 3175), being obtained.

The production of this compound from glyoxylic acid phenylhydrazone and benzenediazonium chloride has also been observed (Busch and others, *Ber.*, 1925, **58**, 442; 1926, **59**, 1162). Its formation in our experiments could not be due to the glyoxylic acid, since this cannot give a hydrazone with benzenediazonium chloride, and the reduction of the latter to phenylhydrazine appears most unlikely. No hydrogen formazyl was produced when the diazonium salt was added to mixtures of glyoxylic acid and the inorganic salts of the medium. Further, in no case during these experiments have we been able to detect the presence of glyoxylic acid before the formation of malonic acid.

The presence of malonic acid in the citric acid cultures has, however, been confirmed in a most satisfactory manner (*a*) by the method of Bougault (*J. Pharm. Chim.*, 1913, **8**, 289; *Ann. chim. anal.*, 1918, **23**, 154), cinnamylidenemalonic acid being isolated, and (*b*) by isolation of the free acid from its lead salt obtained from the evaporated culture.

Many attempts to detect acetonedicarboxylic acid in the citric acid cultures by the use of benzenediazonium chloride, with which it reacts readily (von Pechmann and Jenisch, *Ber.*, 1891, **24**, 3257; Henle and Schapp, *Ber.*, 1905, **38**, 1372), were unsuccessful. In one experiment, a reddish-purple coloration was produced on addition of ferric chloride.

Nevertheless, the transient formation of this acid seems indicated by the fact that on about the seventh or eighth day, *i.e.*, in the early stages of the fermentation, the citric acid–Molliard medium, although giving no ferric chloride reaction, contains acetone. The iodoform reaction, a red colour with alkaline sodium nitroprusside, and a white precipitate with acidified mercuric sulphate (Denigès's solution, *Ann. Chim. phys.*, 1899, **18**, 384) are obtained. Denigès (*loc. cit.*) gives the composition of the wet precipitate as $6HgSO_4,9HgO,4C_3H_6O$. This was decomposed with sodium iodide (Biilmann, *Ber.*, 1902, **35**, 2584), and the acetone characterised as the dibenzylidene derivative and as the *p*-nitrophenylhydrazone.

This appears to be the first recorded instance of the production of acetone by a mould, the well-known fermentation processes for its manufacture (Fernbach and Strange, E.P. 1912, 21073; Gill, *J. Soc. Chem. Ind.*, 1919, **38**, 273T; Speakman, *ibid.*, 155T; *J. Biol. Chem.*, 1920, **41**, 319) depending on the use of bacteria. The authors hope shortly to describe the results of some large-scale experiments. Owing to our failure to detect acetonedicarboxylic acid, it appeared possible that the acetone might arise from acetic acid. It should be mentioned, however, that, apart from an unconfirmed observation recorded by Heinze (*Annales mycologici,* 1903, **1**, 350), acetic acid has not been found in *Aspergillus niger* cultures on sugar or citric acid. Reilly, Hickinbottom, Henley, and Thaysen (*Biochem. J.*, 1920, **14**, 229) and Bakonyi (*Biochem. Z.*, 1926, **169**,

125) have shown that addition of acetic acid to the cultures increases the yield of acetone in the technical fermentation processes.

When grown on a solution of calcium acetate and the usual inorganic salts, *A. niger* gave no acetone, but formed glyoxylic, glycollic, and oxalic acids. The last acid was found by Raistrick and Clark (*loc. cit.*), the others have not previously been identified in this connexion. Dr. P. W. Clutterbuck has suggested to us that on analogy with oxidation processes in the animal organism, acetic acid is probably directly oxidised to glyoxylic acid, which, by dismutation, *i.e.*, the Cannizzaro reaction (Neuberg, *Ber.*, 1922, **55**, 3628), yields oxalic and glycollic acids.

The rapid disappearance of acetone from the citric acid cultures suggested a study of the action of the mould on this substance, but the suitable conditions for growth have not yet been ascertained.

The importance of saccharic acid in the sugar–citric acid fermentation has already been mentioned. Butkewitsch (*Biochem. Z.*, 1923, **142**, 205) was, however, unable to convert it into citric acid by *A. niger*, but this does not necessarily preclude its participation in the process. The conditions under which gluconic acid is converted into citric acid were only established after many failures (see p. 201) and it is possible that Butkewitsch was not working under the optimum conditions.

The authors find that when the mould has been grown on dipotassium saccharate for 4 to 5 weeks the culture gives a precipitate with mercuric sulphate and acidified potassium permanganate—Denigès's test—thus rendering the presence of citric acid probable. When the culture was distilled with potassium permanganate and dilute sulphuric acid, acetone was easily recognised in the distillate. Malic acid and ketonic acids give precipitates with mercuric sulphate and acidified potassium permanganate, but citric, acetoacetic, or acetonedicarboxylic acid would yield acetone on oxidation. The last two acids were shown to be absent. Aconitic acid gave no acetone on similar oxidation. Further work is necessary, however, before the production of citric acid from saccharic acid may be regarded as definitely established.

EXPERIMENTAL.

The medium employed throughout this research contained the following quantities (in grams) of hydrated salts per litre of water : ammonium nitrate, 0·356; potassium dihydrogen phosphate, 0·08; magnesium sulphate, 0·08; ferrous sulphate, 0·0046; zinc sulphate, 0·0046. This medium is hereafter designated solution M.

The fermentations were conducted in large flasks fitted with tubes for the withdrawal of samples under aseptic conditions. All the mixtures were sterilised prior to inoculation, and great care was taken to prevent possible contamination by adventitious organisms. The cultures used for inoculation were all derived from Professor Neuberg's original strain, and when the work had been in progress for seven months, samples from one of the large reaction flasks were kindly examined by Miss M. Rhodes of the Lister Institute and certified as pure. All results were checked by control experiments performed simultaneously under identical conditions.

Fermentation of Citric Acid. Detection of Glyoxylic Acid.—Citric acid (50 g.) in 2500 c.c. of solution M was inoculated and incubated at 30°, and samples were tested frequently for glyoxylic acid. On the seventeenth day, a strong reddish-violet colour was obtained with naphtharesorcinol and hydrochloric acid, whereupon 2000 c.c. of the solution were withdrawn, filtered, and treated with 3 g. of aminoguanidine acetate in 100 c.c. of dilute acetic acid (1 : 1), giving after 48 hours a pale yellow solid (0·05 g.). On recrystallisation, this had m. p. 154° and melted at the same temperature in admixture with an authentic specimen of the aminoguanidine derivative of glyoxylic acid (Found by microanalysis: N, 37·4. Calc.: N, 37·9%). Döbner and Gärtner (*loc. cit.*) give the m. p. of this compound as 161°. Dakin (*J. Biol. Chem.*, 1906, 1, 271) states that the compound does not melt very sharply, but after drying at 100° it has m. p. about 155°. The present authors find that the m. p. depends to some extent on the rate of heating.

Fermentation of Malonic Acid. Detection of Glyoxylic Acid.—Malonic acid (25 g.) in 2500 c.c. of solution M was inoculated and incubated at 30°. On the seventeenth day, a positive naphtharesorcinol test was obtained and 1000 c.c. of the filtered solution were then treated with 2 g. of aminoguanidine acetate and 50 c.c. of glacial acetic acid. After 48 hours, the deposit was separated (0·08 g.). It melted at 152·5°, and at 154·5° after recrystallisation from hot water. A mixture with a synthetic specimen (m. p. 155°) melted at 155° (Found : N, 37·5, 37·5%).

Fermentation of Citric Acid. Detection of Malonic Acid.—Citric acid (30 g.) in 2000 c.c. of solution M was inoculated and incubated at 30° and samples were tested daily with benzenediazonium chloride. On the eleventh day, a red precipitate was obtained, whereupon 600 c.c. of the fermenting liquid were filtered, cooled to 0°, and mixed with a well-cooled solution of benzenediazonium chloride (from 3 g. of aniline) in presence of excess of sodium acetate. After 24 hours, the red solid (2·9 g.) was washed with cold water, dried in a vacuum, and repeatedly crystallised alternately from aqueous methyl alcohol and benzene–light petroleum; it then melted at 118—120°, alone or mixed with an authentic sample of hydrogen formazyl, m. p. 119°. It gave the characteristic dark green coloration with sulphuric acid (Bülow reaction) (Found : C, 69·7, 69·9; H, 5·5, 5·5; N, 25·2, 25·45. Calc. : C, 69·6; H, 5·4; N, 25·0%).

In another experiment, 2000 c.c. of the culture gave, on the tenth day, 1·3 g. of crude hydrogen formazyl.

Fermentation of Citric Acid. Isolation of Malonic Acid.—Citric acid (30 g.) in 2000 c.c. of solution M was inoculated and incubated as before. Malonic acid was detected on the tenth day, the whole of the solution (1900 c.c.) was filtered and concentrated under diminished pressure to 400 c.c., pure sodium carbonate added, and the slight excess neutralised with acetic acid. On evaporation, 43 g. remained, and 24 g. of this were well stirred with 60% alcohol in successive quantities of 25, 15, 15, and 10 c.c., and the extracts were evaporated. The residue (3·4 g.) was free from oxalate and citrate. When it was warmed with acetic anhydride and diluted with glacial acetic acid, the brown solution showed a strong greenish-red fluorescence—a reaction of malonic acid (Kleeman, *Ber.*, 1886, **19**, 2030). 1·5 G. were heated with 2 c.c. of glacial acetic acid and 30 drops of cinnamaldehyde in a sealed tube for 11 hours at 100°. Water (20 c.c.) and sodium carbonate were added, unchanged aldehyde was extracted with ether, and the alkaline solution was acidified, giving 0·6 g. of cinnamylidenemalonic acid. After recrystallisation, this melted at 207° and did not depress the m. p. (207°) of an authentic specimen. On exposure to light, it was superficially converted into a white solid (0·0214 and 0·0388 required 7·8 and 14·2 c.c. of *N*/40-NaOH. Calc., 7·85, 14·25). The alcoholic extract from the remainder (19 g.) of the evaporated culture was precipitated with aqueous lead acetate, and the lead salt decomposed by hydrogen sulphide. The white residue obtained on evaporation of the final filtrate gave, on extraction with ether, malonic acid (m. p. and mixed m. p. 132—133°, decomposing a few degrees above this temperature) (0·1002 and 0·1021 required 38·6 and 39·3 c.c. of *N*/20-NaOH. Calc., 38·55, 39·30).

Fermentation of Citric Acid. Detection of Acetone.—Citric acid (45 g.) in 2500 c.c. of solution M was fermented as usual and samples were tested daily for acetone by the iodoform reaction. This was given very faintly on the sixth day and strongly on the seventh day; 2200 c.c. of the solution were then filtered and neutralised with sodium hydroxide, and distilled. This distillate (800 c.c.) was mixed with 2000 c.c. of Denigès's reagent (50 g. of mercuric oxide in 1000 c.c. of water and 200 c.c. of sulphuric acid), and the whole heated under reflux at 100° for 40 minutes. The white precipitate was separated, washed, dried (90 g.), and distilled, in portions of 15 g., with sodium iodide (30 g.) in 120 c.c. of water; 15 c.c. of distillate were collected in each case. A portion (55 c.c.) of the united distillates was mixed with acetone-free alcohol (60 c.c.), benzaldehyde (3 c.c.), and 10% sodium hydroxide solution (3 c.c.). The condensation product separated over-night and, after crystallisation from light petroleum, melted at 113° alone or in admixture with dibenzylideneacetone (Found: C, 86·6; H, 6·04. Calc.: C, 87·2; H, 6·0%).

The remainder of the distillate (35 c.c.) from the mercury compound was treated with *p*-nitrophenylhydrazine acetate; the product, after crystallisation from light petroleum, was identified as acetone-*p*-nitrophenylhydrazone by its m. p. (148·5°) and by the m. p., 149°, of a mixture with an authentic specimen.

Fermentation of Calcium Acetate. Detection of Glyoxylic Acid.—Calcium acetate (20 g.) in solution M (2000 c.c.) was inoculated and incubated at 32°. Glyoxylic acid made its appearance on the fifteenth day. 700 C.c. of the medium were then removed and filtered, made faintly acid to litmus with hydrochloric acid, neutralised with potassium hydroxide, and treated with 3·5 g. of aminoguanidine acetate in 50 c.c. of glacial acetic acid. After 5 days, 0·42 g. of crude condensation product was obtained. Two crystallisations from much hot water yielded 0·25 g. of m. p. 154° and mixed m. p. 154—155°.

Fermentation of Calcium Acetate. Isolation of Calcium Oxalate.—The remainder of the culture solution gradually deposited a white solid on the sides of the flask, and on the eighteenth day the mycelium was collected on a filter. The adhering solid was removed from the glass by warm 10% hydrochloric acid, which was then used for extracting the mycelium. The united extracts and washings (150 c.c.) were treated with a slight excess of ammonia, boiled for a few minutes, cooled, treated with a slight excess of 10% calcium chloride solution, and again boiled. The precipitate was well washed with much hot water and dried (Found: CaO, 43·9. Calc.: CaO, 43·75%).

Fermentation of Calcium Acetate. Isolation of Glycollic Acid.—Calcium acetate (60 g.) in 4000 c.c. of solution M showed, on the tenth day after inoculation, the presence of glycollic acid. Sulphuric acid, acetic acid, and 5% alcoholic *p*-cresol gave a dark green colour, whilst with sulphuric acid and alcoholic codeine (5%) a characteristic strong pink colour was obtained (Denigès, *Ann. Chim. phys.*, 1909, **18**, 178). The whole of the culture was filtered, treated with 60 g. of oxalic acid, this quantity being in large excess of that required to precipitate the calcium, and the deposit was separated and well washed. The filtrate, containing acetic acid, excess of oxalic acid, and presumably glycollic acid, was treated with lead carbonate. The filtrate from the lead oxalate, containing the soluble lead salts, was treated with hydrogen sulphide, filtered, and evaporated to a syrup in a vacuum. This yielded 5·7 g. of white, transparent crystals, m. p. 68°, which were free from oxalic acid. After two crystallisations from dry ether–light petroleum, these melted at 79—80°, were indistinguishable in appearance from glycollic acid, and did not depress the m. p. (79—80°) of an authentic specimen (0·0508 required 13·40 c.c. of *N*/20-NaOH. Calc., 13·35 c.c. Found: C, 31·7; H, 5·2. Calc.: C, 31·6; H, 5·3%).

Fermentation of Potassium Saccharate. Detection of Citric Acid.—Potassium hydrogen saccharate (10 g.) was exactly neutralised by dilute aqueous potassium hydroxide, the usual inorganic salts were added in the proportions required by medium M, and the solution was diluted to 500 c.c., inoculated, and incubated at 31°. After being kept for 28 days at this temperature and for about a week at 20°, the solution gave a white precipitate with acidified mercuric sulphate solution and potassium permanganate, indicating the probable presence of citric acid.

200 C.c. of the culture were then acidified with sulphuric acid, slowly treated with aqueous potassium permanganate to oxidise any citric acid to acetonedicarboxylic acid, and slowly distilled. The distillate (50 c.c.), when heated with 200 c.c. of Denigès's mercuric sulphate solution (see p. 206), gave 3·8 g. of a white solid; this was distilled with 30 c.c. of water and 8 g. of sodium iodide. The distillate (5 c.c.), treated with 5 c.c. of alcohol, 5 drops of benzaldehyde, and 5 drops of 10% sodium hydroxide solution, gave dibenzylideneacetone, m. p. and mixed m. p. 113° (Found: C, 86·5; H, 6·1. Calc.: C, 87·2; H, 6·0%).

Potassium saccharate gave no acetone on similar oxidation. Distillation of the fermented medium gave no acetone, thus excluding the presence of acetoacetic and acetonedicarboxylic acids. Aconitic acid (5 g.) in 120 c.c. of dilute sulphuric acid (1 : 5) was oxidised with 200 c.c. of 3% potassium permanganate solution; the distillate (20 c.c.) gave only a minute trace of a precipitate when warmed under reflux with acidified mercuric sulphate.

The acetone obtained from the saccharate culture would therefore appear to have arisen from citric acid.

The expenses of this investigation have been in part defrayed by a grant from the Government Grant Committee of the Royal Society, for which the authors desire to express their thanks.

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[*Received, November 20th*, 1926.]

XXXIII.—*Dicyanates and Dibenzoates of Triphenylbismuthine and Triphenylstibine.*

By Frederick Challenger and Vera Katharine Wilson.

From a consideration of the stability to heat of halogen and similar derivatives of the type Ph_3BiX_2, it was shown (J., 1926, 1648) that the halogens and pseudo-halogens could be arranged in an electrochemical order almost identical with that deduced by Birckenbach and Kellermann (*Ber.*, 1925, **58**, 786, 2377) from a study of the decomposition potentials of the potassium salts in aqueous solution.

Further evidence is now adduced as to the similarity of the conclusions reached by these entirely different modes of approach. Birckenbach and Kellermann showed that the electronegative properties of these elements and radicals decrease from fluorine thus: F, ONC, OCN, Cl, N_3, Br, CN, SCN, I, SeCN, TeCN. The position of the cyanate radical, OCN, is particularly interesting, since it is widely separated from the thiocyano- and selenocyano-groups. This difference has also been brought to light by a study of the properties of *triphenylbismuthine dicyanate*, $(C_6H_5)_3Bi(OCN)_2$. It is quite stable at the ordinary temperature, in marked distinction to the corresponding dithiocyanate and diselenocyanate, which lose phenyl pseudohalide. Its temperature of decomposition is about 150°, which is very close to that of triphenylbismuthine dichloride. The reaction is probably complex. Phenyl cyanate, Ph–O–CN, which should be produced according to the general equation $Ph_3BiX_2 = Ph_2BiX + PhX$ (J., 1922, **121**, 91), is unknown. If formed, it would doubtless undergo polymerisation and possibly other changes.

In comparing our results with those of Birckenbach and Kellermann, it has been assumed that triphenylbismuthine dicyanate has the normal cyanate structure, $Ph_3Bi(O{\cdot}C{\vdots}N)_2$. Kaufmann and Kögler (*Ber.*, 1926, **59**, 184), from a comparison of the stabilities of the lead halides and pseudohalides, PbX_4, have reached identical conclusions as to the electrochemical order of F, OCN, and Cl, which give relatively stable derivatives. The thiocyanate, iodide and selenocyanate of this type decompose immediately according to the equation $PbX_4 = PbX_2 + X_2$.

The relative electrochemical positions of iodine and thiocyanogen were first investigated by Soderbäck (*Annalen*, 1919, **419**, 283). In aqueous or ethereal solution, an equilibrium exists between K(or Ag)SCN, K(or Ag)I, I_2, and $(SCN)_2$ and the results were inconclusive. Nitrosyl thiocyanate, however, has a transitory existence in the deep red solutions obtained from nitrous acid and thiocyanates, or from nitrosyl chloride and silver thiocyanate. No evidence of the existence of the corresponding iodide can be obtained, but nitrosyl bromide is stable below —2°. On these grounds, he considered iodine to be the more positive radical. By a comparison of the times required for the development of the odour of iodobenzene and phenyl thiocyanate when triphenylbismuthine dichloride is mixed with aqueous solutions of potassium iodide and thiocyanate, results are obtained in agreement with those of Soderbäck and of Birckenbach and Kellermann (compare J., 1926, 1648). The observed times were 3 and 40 seconds, respectively, at the ordinary temperature, the theoretical quantities of the different salts being employed. The slower production of phenyl thiocyanate has been noted on several occasions and, indicating the slower decomposition of the dithiocyanate, is evidence of the more positive nature of iodine.

Wilkinson and one of us have shown (J., 1924, **125**, 856) that nitration of triphenylbismuthine dinitrate yields a meta-derivative. Owing to the oxidation of the triaryl derivatives (R_3M) of bismuth, antimony, arsenic, and phosphorus to compounds of the type $R_3M(O{\cdot}NO_2)_2$ during nitration, it was impossible to determine the orienting influence of the metal or metalloid in the tervalent condition.

From the work of Gelissen and Hermans (*Ber.*, 1925, **58**, 287) it appeared probable that, by the action of benzoyl peroxide on the triphenyl derivatives of the elements of the nitrogen group, mixed organo-derivatives such as $Ph_2Bi{\cdot}C_6H_4{\cdot}Ph$ or

$$PhCO{\cdot}O{\cdot}C_6H_4{\cdot}BiPh_2$$

might be obtained, according to the equations

$$\text{(I.)}\quad (PhCO)_2O_2 + Ph_2M{\cdot}C_6H_5 = PhCO_2H + CO_2 + Ph_2M{\cdot}C_6H_4{\cdot}Ph.$$
$$\text{(II.)}\quad (PhCO)_2O_2 + Ph_2M{\cdot}C_6H_5 = PhCO{\cdot}O{\cdot}C_6H_4{\cdot}MPh_2 + CO_2 + PhH.$$

The first reaction might be expected to predominate (Gelissen).

The dibromide or dichloride of a substance of the type $Ph_2M{\cdot}C_6H_4{\cdot}Ph$ might yield on suitable decomposition a halogen derivative of diphenyl, $C_6H_5{\cdot}C_6H_4X$ (J., 1915, **107**, 21, 23; 1924, **125**, 857): $(Ph{\cdot}C_6H_4)MPh_2X_2 = Ph{\cdot}C_6H_4X + Ph_2MX$. By orientation of the halogen atom in this compound, the directing influence of the tervalent element M might be determined. In boiling light petroleum, however, triphenylbismuthine and benzoyl peroxide gave *triphenylbismuthine dibenzoate*. The corresponding *stibine dibenzoate* was prepared in a similar manner. No other products could be isolated. The two dibenzoates were identical with the compounds obtained from silver benzoate and the bismuthine and stibine dichlorides. Gelissen and Hermans (*Ber.*, 1926, **59**, 666) obtained a dibenzoate from *cyclo*hexene and the peroxide.

Triphenylphosphine and benzoyl peroxide in light petroleum at the ordinary temperature give triphenylphosphine oxide and benzoic anhydride, but no perbenzoic acid could be detected (compare Gelissen and Hermans, *Ber.*, 1926, **59**, 66). This illustrates the great tendency of the phosphorus atom in the phosphines to become quinquevalent, and is analogous to the action of thiocyanogen and thiocyanic acid giving the sulphide, Ph_3PS (J., 1923, **123**, 1054).

Difficulties in the preparation of triphenylphosphine (J., 1924, **125**, 864) may be avoided by using the method of Gilman and Vernon (*J. Amer. Chem. Soc.*, 1926, **48**, 1066), the crude undistilled triphenyl phosphite being treated directly with magnesium phenyl bromide. This method is much less troublesome than that involving the use of sodium and gives a much better yield.

EXPERIMENTAL.

Triphenylbismuthine dicyanate was prepared by shaking the dichloride (2·4 g.; 1 mol.) and silver cyanate (1·4 g.; 2 mols.) in dry ether (40 c.c.) for 4 hours. Extraction of the insoluble residue with chloroform yielded a solid which was crystallised twice from chloroform–light petroleum; m. p. 128·5—129°. A further quantity was obtained from the ether. The weight of silver chloride obtained was 1·30 g. (calc., 1·32 g.) (Found: C, 45·8, 45·8; H, 3·1, 3·2; N, 5·5, 5·4; Bi, 39·4, 39·1. $C_{20}H_{15}O_2N_2Bi$ requires C, 45·8; H, 2·9; N, 5·35; Bi, 39·9%).

When the dicyanate is warmed with aqueous alcohol (1:1), ammonia is evolved. On heating with excess of water, it gives a turbid, frothing liquid resembling an alkaline solution of the dichloride, and probably containing the unstable dihydroxide or oxide (J., 1920, **117**, 765). On heating to 150°, the dicyanate decomposes and an oil with an intensely pungent odour distils and partly solidifies. No definite product could be isolated from the minute amount available.

In one experiment, the silver cyanate used contained carbonate. The silver chloride precipitate then contained some insoluble triphenylbismuthine carbonate, which remained after removal of the dicyanate with chloroform and of silver salts with ammonia. With hydrochloric acid, it gave the dichloride, recognised by m. p. and mixed m. p.

Triphenylstibine Dicyanate.—Triphenylstibine dichloride (3·2 g.) and silver cyanate were shaken in dry ether for 14 hours. The solid was then washed with ether, leaving 2 g. of silver chloride (calc., 2·16 g.). The ether yielded 2·5 g. of white crystals, m. p. 105—113°. After two crystallisations from chloroform–light petroleum, these melted at 111—112° (Found: N, 6·5, 6·4; Sb, 27·4, 28·1. $C_{20}H_{15}O_2N_2Sb$ requires N, 6·4; Sb, 27·9%).

Triphenylbismuthine and Benzoyl Peroxide.—An intimate mixture of these compounds reacted violently at 68°, white fumes and a strong odour of diphenyl being produced. Extraction with hot water and sodium hydroxide and crystallisation of the residue from alcohol yielded triphenylbismuthine and bismuth hydroxide. Other conditions were therefore employed.

The bismuthine (4 g.), benzoyl peroxide (2·2 g.; 1 mol.), and light petroleum (b. p. 60—80°; 50 c.c.) were heated under reflux. The clear solution soon deposited 3·3 g. of a faintly yellow solid, m. p. 164·5—166·5°. This was repeatedly crystallised from benzene–light petroleum, the last three operations giving products of m. p. 171·5–173·5°, 172—173·5°, 171—172·5°, taken simultaneously. The compound decomposed a few degrees above the m. p. With hot hydrochloric acid, it gave no benzene, indicating the absence of tervalent bismuth, but was converted into benzoic acid and triphenylbismuthine dichloride, m. p. 139—141°. When it was mixed with potassium iodide or thiocyanate in aqueous suspension, the characteristic odours of iodobenzene and phenyl thiocyanate were produced, thus affording conclusive proof of the presence of a derivative of quinquevalent bismuth (J., 1922, **121**, 92; 1924, **125**, 854). Analysis showed the substance to be *triphenylbismuthine dibenzoate*, and it did not depress the m. p. of the product obtained from the dichloride and silver benzoate (Found: Bi, 30·8, 30·5. $C_{32}H_{25}O_4Bi$ requires Bi, 30·6%).

The petroleum mother-liquor from the original reaction was concentrated, yielding successively benzoyl peroxide, triphenylbismuthine dibenzoate, and triphenylbismuthine.

Triphenylstibine and Benzoyl Peroxide.—From the stibine (5 g.) and the peroxide (3·4 g.; 1 mol.) in light petroleum (b. p. 60—80°; 100 c.c.), a solid, m. p. 170·5—173·5°, separated after 20 minutes' heating (7·3 g.). After two crystallisations from benzene–light petroleum, it melted at 171·5°, the purification being less troublesome than that of the corresponding bismuth compound. With hot hydrochloric acid, the stibine dichloride (m. p. and mixed m. p. 142—143°) and benzoic acid, m. p. 121°, were obtained. The original petroleum filtrate yielded a trace of triphenylstibine.

Analysis showed the product to be *triphenylstibine dibenzoate*. It did not depress the m. p. (170·5—172·5°) of the compound obtained from the dichloride and silver benzoate (Found: Sb, 20·4, 20·6. $C_{32}H_{25}O_4Sb$ requires Sb, 20·5%).

A comparison of the m. p.'s of the dichlorides and dibenzoates of triphenylbismuthine and triphenylstibine is of interest:

	Dibenzoate.	Dichloride.
Bismuthine	172—173°	141°
Stibine	171—171·5	143

Preparation of the Bismuthine and Stibine Dibenzoates from the Corresponding Dichlorides.—(*a*) Bismuthine dichloride, 2 g.; (*b*) stibine dichloride, 0·9 g. Silver benzoate (2 mols.) (*a*) 1·8 g., (*b*) 0·95 g. Reaction occurred on shaking in chloroform over-night. The product, purified as described above, had m. p. (*a*) 171·5°, (*b*) 170·5—172·5°.

Triphenylphosphine and Benzoyl Peroxide.—The phosphine (2·9 g.) and the peroxide (2·7 g.; 1 mol.) were separately and completely dissolved in light petroleum, and the cold solutions mixed. A precipitate quickly formed which melted at 140—148°, and after three crystallisations from chloroform–light petroleum had the constant m. p. 153·5°. It did not depress the m. p. (153·5°) of an authentic specimen of triphenylphosphine oxide.

The original petroleum filtrate on concentration deposited white crystals, m. p. 37·5—39·5°. These were free from phosphorus (and from perbenzoic acid, as shown by the odour and by the behaviour to both aniline and potassium iodide) and when mixed with benzoic anhydride (m. p. 42·5—43·5°) also melted at 37·5—39·5°. The compounds appeared to be identical. With warm aniline, the product from the reaction quickly gave benzanilide, m. p. and mixed m. p. 159—160°, but no nitrosobenzene.

When the phosphine and the peroxide were shaken in the minimum of light petroleum for an hour, heat was developed. The products of the reaction were the same.

The authors wish to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, November 13th,* 1926.]

XXXIV.—*Acid and Salt Effects in Catalysed Reactions. Part IV. Derivation of a General Equation for the Catalytic Activity of Acids. The General Catalytic Catenary.*

By HARRY MEDFORTH DAWSON.

THE results of experiments described in previous papers (Dawson and Carter, J., 1926, 2282; Dawson and Dean, *ibid.*, p. 2872; Dawson and Hoskins, *ibid.*, p. 3166) show that the catalysing power of acid–salt mixtures of the type $c\mathrm{HA} + x\mathrm{MA}$ (c constant and x variable) is such that, in general, the reaction velocity falls as x increases, reaches a minimum, and then increases continuously according to the linear formula $v = a + bx$. The curves which are obtained by plotting the reaction velocity against the p_{H} value of the catalysing solution are symmetrical with respect to the point at which the velocity is a minimum.

In accordance with the equations for the hydrogen-ion concentration $[\mathrm{H}^+]_i$ and the velocity v_i which characterise the minimum velocity (*M.V.*) mixture, namely,

$$[\mathrm{H}^+]_i = \sqrt{k_a K c/(k_h - k_m)}$$

and

$$v_i = 2\sqrt{(k_h - k_m) k_a K c} + k_m c$$

it has also been shown that for a given acid $[\mathrm{H}^+]_i$ is directly proportional to the square root of the acid concentration, and that the specific minimum velocity v_i/c is a linear function of the square root of the dilution of the acid.

It follows that the reaction velocities for all possible mixtures of an acid with its corresponding salts can be represented on the v–p_{H} diagram by a sheaf of curves which are catenary in type. The dimensions of the individual catenaries and the positions of their apices (the *M.V.* points) are determined by the nature of the acid and its concentration. The influence of the nature of the acid finds expression in the catalytic coefficients, k_h, k_a, and k_m for the hydrogen ion, the acid anion, and the undissociated acid molecule, respectively, and in the ionisation constant, K, of the acid. The catenary curves on the v–p_{H} diagram, it may be noted, should really be considered as the projections on this plane of catenary surfaces, the complete representation of which would necessitate the use of a tridimensional co-ordinate system with reaction velocity, acid concentration, and p_{H} as the respective co-ordinates.

Although the observations already described are such as to suggest that the relations involved are of general character, it may now be pointed out that similar catalytic phenomena have been met with as a result of the preliminary examination of many other acids. Amongst these may be mentioned oxalic acid (both in the first and second stages of dissociation), tartaric acid (first and second stages), phosphoric acid (first and second stages), and sulphuric acid (second stage). In the case of the strongest acids (such as the halogen acids, nitric acid, etc.), there is, however, no initial fall, but, on the other hand, the velocity increases continuously with the concentration of the added salt. It will be shown in due course that this behaviour of the strongest acids is not inconsistent with the views which have been developed on the basis of observations made with weaker acids.

In the circumstances, it seems desirable at this stage to indicate that the theory outlined in the previous papers of this series leads to a general formula for the catalytic effects produced by acids which, in view of its simplicity, would seem to be of considerable importance. This general formula follows directly from the equation

$$v = v_h + v_a + v_m = k_h[\mathrm{H}^+] + k_a[\mathrm{A}^-] + k_m[\mathrm{HA}] \quad . \quad . \quad (1)$$

the only assumption involved being that the dissociation of the acid conforms to the requirements of the mass law. Substituting for $[\mathrm{A}^-]$ the value given by $[\mathrm{A}^-] = K(c - [\mathrm{H}^+])/[\mathrm{H}^+]$ and for $[\mathrm{HA}]$ the value $c - [\mathrm{H}^+]$, and rearranging the terms, we get

$$v = (k_h - k_m)[\mathrm{H}^+] + k_aKc/[\mathrm{H}^+] + k_mc - k_aK \quad . \quad . \quad (2)$$

For a fixed acid concentration, the variations in velocity are due to changes corresponding with the first two terms, and if the ionic reaction velocity is denoted by u, we may write

$$u = v_h + v_a = (k_h - k_m)[\mathrm{H}^+] + k_aKc/[\mathrm{H}^+] \quad . \quad . \quad (3)$$

If the hydrogen-ion concentration $[\mathrm{H}^+]$ is expressed in terms of the hydrogen-ion concentration $[\mathrm{H}^+]_i$ of the corresponding *M.V.* mixture, such that $[\mathrm{H}^+] = n[\mathrm{H}^+]_i$, then equation (3) may be written

$$u = (k_h - k_m)n[\mathrm{H}^+]_i + k_aKc/n[\mathrm{H}^+]_i,$$

and since $[\mathrm{H}^+]_i = \sqrt{k_aKc/(k_h - k_m)}$,

we have $u = \sqrt{(k_h - k_m)k_aKc}\,(n + 1/n) \quad . \quad . \quad . \quad . \quad (4)$

Since, further, the minimum ionic velocity u_i is given by

$$u_i = 2\sqrt{(k_h - k_m)k_aKc} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

we obtain by combination of (4) and (5)

$$r = u/u_i = \tfrac{1}{2}(n + 1/n) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In equation (6), n represents the hydrogen-ion concentration of any solution in terms of that of the corresponding *M.V.* mixture, and may be termed the reduced hydrogen-ion concentration. Similarly, r expresses the velocity due to the hydrogen and acid anions for any solution in terms of the ionic reaction velocity of the corresponding *M.V.* mixture and may be called the reduced ionic reaction velocity.

If $\log_{10} n = (p_{\mathrm{H}})_i - p_{\mathrm{H}}$ be denoted by Δp_{H}, then Δp_{H} may be referred to as the reduced p_{H} value of the solution in question, and equation (6) may be written in the form

$$r = \tfrac{1}{2}(10^{\Delta p_{\mathrm{H}}} + 10^{-\Delta p_{\mathrm{H}}}) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is the equation of a catenary, and it expresses quite generally the connexion between the reduced ionic velocity and the reduced p_H value for any catalysing solution. Its applicability would appear to be independent of the nature and concentration of the catalysing acid, of the temperature, of the nature of the solvent, and also of the nature of the catalysed reaction. It is therefore to be regarded as a general formula applicable to all catalysed reactions in so far as the velocity of these depends on the positive hydrogen ions and the corresponding negative anions.

It follows that the ionic reaction velocities for any acid-catalysed reaction should be representable by a single catenary curve. Equation (7) and the corresponding curve obtained by plotting the reduced ionic reaction velocity against the reduced p_H value may be termed the reduced or general catalytic catenary.

It may be noted that, in the derivation of this relation, the procedure followed is analogous to that by which the specific gas equations of the ordinary type are transformed into general reduced equations of condition.

The mathematical form of the general equation may be further simplified, for if the natural logarithm of the reduced hydrogen-ion concentration is denoted by h, *i.e.*, if $\log_e n = h$, then this equation may be written

$$r = \cosh h \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

according to which, the reduced ionic velocity is equal to the hyperbolic cosine of the logarithm of the reduced hydrogen-ion concentration. There are obvious reasons, however, for regarding equation (7) as the more convenient form of the general relation.

Significance of the Reduced Catalytic Catenary.

The experimental data on which the foregoing views are based have reference to the catalytic behaviour of acid–salt mixtures represented by $c\mathrm{HA} + x\mathrm{MA}$, in which c is constant and x is variable. In accordance with the view that the salt is completely ionised, this series of mixtures may be represented by $c\mathrm{HA} + x\mathrm{A}^-$, for the positive ion M^+ has no measurable catalytic activity.

The symmetry of the reduced catalytic catenary obviously suggests the possibility of a complementary series corresponding with the formula $c\mathrm{HA} + x'\mathrm{H}^+$, but it does not follow that the latter can be actually realised, for although it is very probable that the strongest acids are very largely ionised, there is evidence to support the view that the ionisation is not complete. Since the non-ionised acid would appear to be a very active catalyst, it is clear that there may be a considerable difference in practice between the two stoicheiometrically complementary series of solutions.

If, however, it is assumed that the ionisation of a strong acid, *e.g.*, hydrochloric acid, is practically complete in dilute solution, and that the catalytic activity of the chlorine ion is negligible in comparison with that of the hydrogen ion, it should be possible to realise to a limited extent the series of solutions which is represented by $c\mathrm{HA} + x'\mathrm{H}^+$.

The dividing line between the stoicheiometrically complementary series of catalysing solutions corresponds with $x = x' = 0$. This corresponds with a solution of the free acid HA and it may be shown that this is represented by a point on the reduced catalytic catenary, the position of which is determined solely by the relative magnitudes of the catalytic coefficients k_h, k_a, and k_m.

It will be assumed that the acid concerned is weak and that the hydrogen-ion concentration $[\mathrm{H}^+]_0$ of the pure acid solution is given with sufficient exactness by the mass-law expression $[\mathrm{H}^+]_0 = \sqrt{Kc}$. We may then write

$$u_0 = (k_h - k_m)\sqrt{Kc} + k_a\sqrt{Kc},$$

and since

$$u_i = 2\sqrt{(k_h - k_m)k_aKc},$$

we obtain by division

$$r_0 = u_0/u_i = \tfrac{1}{2}(\sqrt{(k_h - k_m)/k_a} + \sqrt{k_a/(k_h - k_m)}) \quad . \quad . \quad (8)$$

where r_0 denotes the reduced ionic velocity for the pure acid solution.

From equations (6) and (8) it is apparent that the reduced ionic concentration of solutions of the pure acid is given by $n_0 = \sqrt{(k_h - k_m)/k_a}$, whence

$$(\Delta p_{\mathrm{H}})_0 = \log_{10}\sqrt{(k_h - k_m)/k_a} \quad . \quad . \quad . \quad . \quad (9)$$

It is thus evident that the position of the point H_0 on the catenary is determined by the magnitude of the catalytic coefficients for the acid in question.

Since the relative magnitudes of the catalytic coefficients vary widely according to the strength of the acid and according to the nature of the catalysed reaction, it is obvious that the experimental realisation of the catenary curve may be achieved much more readily with some reactions than it is with others. For such reactions as ester hydrolysis and sucrose inversion, it would seem that the coefficients k_a and k_m are very small in comparison with k_h.

According to the evidence which is available for the acetone-iodine reaction, k_m can be neglected in comparison with k_h in the case of weaker acids, whilst the ratio k_h/k_a increases with increasing strength of the acid as measured by the dissociation constant K.

Catalytic Effects due to the Hydrogen and Hydroxyl Ions.

In accordance with the very general character of the reduced catalytic catenary, it is not surprising that the catalytic effects produced by the simultaneous action of the hydrogen and hydroxyl ions should conform to the requirements of equation (7). This, indeed, may be regarded as a particular case of catalytic action in which the hydrogen ion and the acid ion (hydroxyl) are derived from or are controlled by the solvent.

The equation for the velocity of reaction may be written

$$v = k_h[H^+] + k_{OH}[OH^-] + k_m[H_2O],$$

and since $[H^+].[OH^-] = K_w$ and $[H_2O]$ is constant, it follows that the ionic velocity u is given by

$$u = k_h[H^+] + k_{OH} . K_w/[H^+].$$

The reaction velocity is a minimum when the hydrogen-ion concentration has the value $[H^+]_i = \sqrt{k_{OH} . K_w/k_h}$. Substituting this in the equation for u we obtain

$$u_i = 2\sqrt{k_h . k_{OH} . K_w},$$

whence

$$\begin{aligned} r &= \tfrac{1}{2}([H^+]/[H^+]_i + [H^+]_i/[H^+]) \\ &= \tfrac{1}{2}(n + 1/n) \\ &= \tfrac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H}), \end{aligned}$$

or the same result as that which was obtained for the reduced ionic velocity due to the joint catalytic effect of any acid HA in conjunction with the corresponding salt.

In view of the very weak acidic character of water, it is probable that the magnitude of the coefficient k_m is very small in comparison with k_h and k_{OH}, in which case the ionic velocity u is identical with the actually measured velocity v.

The main difference between the catalytic effects which are produced by the combined action of the hydrogen and hydroxyl ions, as compared with those which have been observed for the catalysing action of acid–salt mixtures in the acetone–iodine reaction, lies in the fact that k_{OH}/k_h is greater than unity, whilst for the acids used in the acetone experiments k_a/k_h is less than unity.

A reaction in which the joint action of hydrogen and hydroxyl ions has been studied is the hydrolysis of methyl acetate at 25°, for which, according to Wijs (*Z. physikal. Chem.*, 1893, **11**, 492; **12**, 514), the value of k_{OH}/k_h is about 1400, and since the hydrogen-ion concentration corresponding with minimum reaction velocity is given by $[H^+]_i = \sqrt{k_{OH}K_w/k_h}$, it follows that $(p_H)_i = 5{\cdot}43$ if K_w is equal to 10^{-14}. The neutral point characterised by $p_H = 7$ lies, therefore, on the right-hand side of the catalytic catenary. In these circumstances, it is obvious that the addition of acid ion (hydroxyl) in the form of, say, sodium hydroxide to pure water will not diminish, but on the contrary, will increase the reaction velocity, and that the attainment of the *M.V.* point will necessitate the diminution of the hydroxyl-ion concentration by the addition of hydrogen ions. The so-called neutral point for water corresponds in the more general case with a solution of the free acid HA, the hydrogen-ion concentration of which has already been denoted by $[H^+]_0$. The H_0 points are characterised by equality of the concentrations of the hydrogen ion and the corresponding anion, whereas the H_i points are distinguished by the equality of the catalytic effects which are produced by the positive and negative ions. Since $(\Delta p_H)_0 = \frac{1}{2} \log (k_h - k_m)/k_a$, it is clear that the H_0 point will be situated on one branch of the catalytic catenary if the ratio $(k_h - k_m)/k_a$ is greater than unity, and on the other branch if the ratio is less than unity. When k_m can be neglected in comparison with k_h, the relative positions of the H_0 and H_i points will be determined by k_h/k_a.

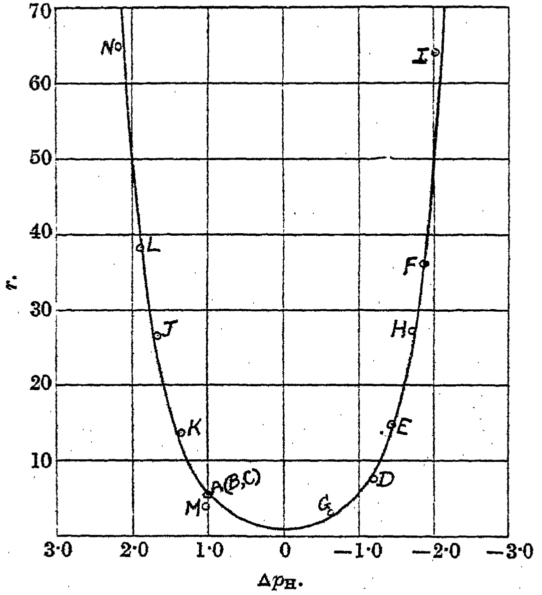
The relations described point strongly to the undesirability of differentiating between the hydroxyl ion and other acid ions. The catalytic behaviour of the hydroxyl ion is indeed so closely similar to that of other acid ions that there appears to be no valid reason for the commonly accepted view that the hydroxyl ion is distinguished from other negative ions in its catalytic properties. In due course, experiments will be described which show directly that negative ions, other than hydroxyl, have very highly developed catalytic activity.

Testing the Reduced Catalytic Catenary.

The data available for submitting the general catalytic catenary to the test of experiment are limited to those furnished by observations on the velocity of the acetone–iodine reaction and to Karlsson's data (*Z. anorg. Chem.*, 1921, **119**, 69) for the rate of hydrolysis of methyl and ethyl acetates at 85·5° in aqueous solutions buffered by the addition of mixtures of acetic acid and sodium acetate. The p_H values of these buffered solutions were determined electrometrically at 85·5° and from a series of observations with each of the two esters Karlsson has derived the minimum reaction velocities and the corresponding $(p_H)_i$ values, a knowledge of which is required for the purpose of the test.

Critical inspection of Karlsson's data shows that the accuracy attained in the individual experiments is not of a high order, and for this reason it is only possible to consider those observations in which the effect of errors of experiment is as small as possible. Whatever the nature of the catalysed reaction, the nearer we approach the apex of the catalytic catenary, the more accurate must be the measurements if they are to be utilised for the purpose of testing the general equation which has been derived.

The accompanying diagram shows the general catalytic catenary with r as ordinate and Δp_H as abscissa. The points shown on the diagram and indicated by capital letters refer to experimental observations, the nature of which is summarised in the table on



The general or reduced catalytic catenary.

p. 221. Subject to the above consideration, the observations have been selected from the available material so as to cover as wide a range as possible. In the case of the acetone–iodine reaction—points A to K—the observations include data for both acetic and chloroacetic acids in the presence and absence of the corresponding salts. The table gives the values of p_H, $(p_H)_i$, v, v_i, u, and u_i, from which the required values of Δp_H and r have been computed. The numbers expressing the reaction velocities are the actual velocities in g.-mols. per litre per minute multiplied by 10^6. Karlsson's numbers have therefore been multiplied by 2·30.

In reference to the table of results it should be noted that the data for the 0·05, 0·1, and 0·2N-acetic acid solutions (points A, B, and C) give values for r and Δp_H which are identical within the limits of

TABLE I.

Characterisation of the Points included in the Diagram of the General Catalytic Catenary.

Nature of catalyst or catalysed reaction.	p_H.	$(p_H)_i$.	Δp_H.	v.	v_i.	u.	u_i.	r.
A. 0·05N-$CH_3\cdot CO_2H$.	3·01	4·03	+1·02	0·50	0·164	0·425	0·089	4·8
B. 0·1N-$CH_3\cdot CO_2H$.	2·87	3·88	+1·01	0·75	0·273	0·60	0·123	4·9
C. 0·2N-$CH_3\cdot CO_2H$.	2·72	3·72	+1·00	1·16	0·465	0·86	0·165	5·2
D. 0·05N-$CH_3\cdot CO_2H$ + 0·16N-$CH_3\cdot CO_2Na$.	5·24	4·03	−1·21	0·724	0·164	0·649	0·089	7·3
E. 0·1N-$CH_3\cdot CO_2H$ + 0·4N-$CH_3\cdot CO_2Na$.	5·33	3·88	−1·45	1·95	0·273	1·80	0·123	14·6
F. 0·1N-$CH_3\cdot CO_2H$ + 1N-$CH_3\cdot CO_2Na$.	5·73	3·88	−1·85	4·60	0·273	4·45	0·123	36·2
G. 0·2N-$CH_3\cdot CO_2H$ + 0·1N-$CH_3\cdot CO_2Na$.	4·33	3·72	−0·61	0·775	0·465	0·475	0·165	2·9
H. 0·2N-$CH_3\cdot CO_2H$ + 1N-$CH_3\cdot CO_2Na$.	5·43	3·72	−1·71	4·80	0·465	4·50	0·165	27·2
I. 0·2N-$CH_3\cdot CO_2H$ + 2N-$CH_3\cdot CO_2Na$.	5·73	3·72	−2·01	10·9	0·465	10·6	0·165	64
J. 0·1N-$CH_2Cl\cdot CO_2H$.	1·91	3·56	+1·65	7·75	2·60	5·35	0·20	26·7
K. 0·1N-$CH_2Cl\cdot CO_2H$ + 0·02N-$CH_2Cl\cdot CO_2Na$.	1·21	3·56	+1·35	5·12	2·60	2·72	0·20	13·6
L. Hydrolysis of methyl acetate.	2·83	4·70	+1·87	1220	32	1220	32	38
M. Hydrolysis of methyl acetate.	3·69	4·70	+1·01	122	32	122	32	3·8
N. Hydrolysis of ethyl acetate.*	2·85	5·05	+2·20	980	15	980	15	65

* The values assigned by Karlsson to $(p_H)_i$ and u_i for the hydrolysis of ethyl acetate are 5·10 and $6{\cdot}8 \times 10^{-6}$, respectively. The values adopted in the table are 5·05 and $6{\cdot}5 \times 10^{-6}$, which would appear to be more nearly in accordance with the graph of Karlsson's experimental data.

error. This result is entirely in accordance with equations (8) and (9), which give respectively $r = 5{\cdot}0$ and $\Delta p_H = 0{\cdot}99$, values which are independent of the concentration of the acid.

Having regard to the nature of the variations which are represented in the table and on the diagram—variations in the nature of the catalysed reaction, in the nature and type of the catalyst, and in the temperature of the respective observations—the concordance between the experimental data and the theoretical deductions is such as to justify the belief that the reduced catalytic catenary represents a very general expression for the effects produced by the joint action of the catalytically active ions which are formed by the dissociation of acids.

Finally, it may be noted that the movement of an index point along the general catenary from left to right represents, not only the changes in catalytic activity which are produced by the addition of a salt to the corresponding acid, but also a continuous series of H_0 points corresponding with pure acids for which the relative catalytic activity of the acid anion increases whilst the ionisation constant decreases.

Summary.

A general equation for the velocity of chemical change has been derived which expresses the catalytic effects produced by acids, either alone or in the presence of the corresponding salts.

This equation may be written in the form

$$r = \tfrac{1}{2}(10^{\Delta p_{H}} + 10^{-\Delta p_{H}}),$$

in which r is the velocity due to the positive and negative ions expressed in terms of the velocity for the corresponding *M.V.* mixture, and Δp_H is the difference between the p_H values of the solution in question and of the *M.V.* mixture.

The above expression, which corresponds with a catenary curve, may be termed the general or reduced catalytic catenary. It appears to be capable of very wide application and is independent of the nature of the catalysing acid, of its concentration, of the temperature, of the nature of the solvent, and of the type of the catalysed reaction.

The general catalytic catenary has been tested by reference to the data which are available for the purpose.

UNIVERSITY OF LEEDS. [*Received, November 24th,* 1926.]

XXXV.—*The Liesegang Phenomenon and Stratification.**

By MAURICE COPISAROW.

THE present study of colloidal and stratified calcium carbonate, not only completes the investigation on the heteromorphism of this substance (J., 1923, **123**, 785), but also shows that neither organised life nor organic hydroxy-compounds, and—more remarkable still—neither colloid, at least of a permanent character, nor suspended matter, is essential in the formation of strata. Nevertheless, although only hydration is necessary for the stratification of calcium carbonate, yet, as is shown later, the presence of colloids and salts and experimental conditions, such as temperature and pressure, which influence hydration, greatly affect the nature of the product. Thus, whilst hydrocalcite ($CaCO_3,5H_2O$) (Copisarow, *loc. cit.*) represents the maximum state of hydration under normal conditions, a hexahydrate is obtained in sugar solution, etc. (Pelouze, *Compt. rend.*,

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* Publication of this work, which was carried out during 1923—24, long before the appearance of Ganguly's paper (J., 1926, 1381), has been delayed owing to the illness of the author.

1865, **60**, 429; Mackenzie, J., 1923, **123**, 2409). Again, whilst ordinarily the dehydration of calcium carbonate * is complete at 18—20°, yet in the case of mother-of-pearl (formed in presence of "conchiolin") apparently a dihydrate persists up to 50°, at which temperature the mother-of-pearl loses its iridescence, becoming "dead." †

Cohesion, hitherto elusive, not only in synthetically prepared calcium carbonate of the stratified variety, but also in all cases of Liesegang ring formation, is certainly dependent upon velocity of formation and pressure. The influence of pressure upon cohesion is well illustrated by the synthesis of marble and alabaster (Copisarow, *loc. cit.*). Unfortunately, owing to lack of facilities, the study of pressure and the time factor upon Liesegang rings in general, and rings of calcium carbonate in particular, could not be carried out.

Considering the peculiarities of the stratification of calcium carbonate itself, we find that it is the first case in which (*a*) Liesegang rings, (*b*) opacity bands, and (*c*) tree formation make a joint appearance. This combination of occurrences may be regarded as an extension of the Liesegang phenomenon, rather than an anomaly of it.

The fibrillar structure of the colloidal calcium carbonate formed *in situ* supplies the necessary framework for the ring formation, and at the same time accounts for its peculiar physical properties. The presence of colloidal calcium carbonate and the general mild conditions explain the formation of opacity regions, which, being the outcome of the mild effect of an electrolyte upon a colloid, may be regarded as very diffused Liesegang rings. This formation of opacity bands of colloidal calcium carbonate (the concentrations of which progress in opposite directions to one another) is identical with the observations of Holker (*Proc. Roy. Soc.*, 1923, *A*, **102**, 710), the distinguishing feature between the two being that Holker's whole series of test-tube experiments is naturally embodied in one phenomenon, taking place in one vessel. The tree formation, as an extreme case of spiral deformation of Liesegang rings, may be regarded as being due, on the one hand, to strong diffusion and, on the other, to the transformation of a semipermeable membrane to an impermeable one owing to the dehydration of calcium carbonate. In this case, diffusion takes place at one or more points of least resistance instead of throughout the whole membrane.

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* Hydrocalcite, $CaCO_3,5H_2O$ (Pfeiffer, *Arch. Pharm.*, 1879, **15**, 212; Copisarow, *loc. cit.*), and subhydrocalcite, $CaCO_3,3H_2O$ (Ivanow, *Z. Kryst. Min.*, 1908, **44**, 87; Copisarow, *loc. cit.*), are the only mineral hydrated forms of calcium carbonate. $CaCO_3,2H_2O$ (mother-of-pearl ?) and $CaCO_3,6H_2O$ are formed in presence of organic matter only.

† Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) gave the following analysis of mother-of-pearl :

$CaCO_3$, 75; H_2O, 25; albumin, 5% ($CaCO_3,2H_2O$ requires H_2O, 26·7%).

Extremes in reactivity and in conditions of experiment are detrimental to the periodic effect. The electrolyte, to be effective, must be strong enough to cause orientation, coagulation, or "salting out" in the medium (electrolyte, colloid, or matter in suspension). Opacity bands, produced by salt solutions acting upon colloids (Holker, *loc. cit.*), by ammonia gas upon gelatin (see later), and by the interaction of calcium chloride with sodium carbonate, indicate the phenomenon of periodicity, but are not strong enough to condense these wide bands to a series of rings or membranes.

The Liesegang phenomenon is complex in character, and the actual rings are the outcome of a primary and a secondary cause. The primary cause is the periodic deformation or coagulation of the fibrillar structure of the colloid, under the influence of the electrolyte. The secondary cause, contributing to the viscosity and thickness rather than to the formation of the rings, is the salting out or deposition of the electrolyte on the coagulated membrane. Thus the usual Liesegang rings represent an intimate mixture of electrolyte and colloid. The fact that the secondary cause may be eliminated without interfering with the first or periodic effect, is shown by the action of hydrochloric acid, ammonia, or formaldehyde on gelatin, described later. Not infrequently, cases are encountered where the initial substances taking part in the Liesegang formation are neutral in character, but in these cases we often find hydrolysis or reduction preceding ring formation, acidic or basic bodies being produced *in situ*.

The general study of the Liesegang phenomenon in this paper revealed the possibility of substituting in ring formation the two salt and the one salt–acid systems (Moeller, *Kolloid Z.*, 1917, **20**, 242) by (1) one basic salt (sodium carbonate, baryta, etc.), and (2) a gas or its aqueous solution (hydrogen chloride, formaldehyde, ammonia, etc.).

These facts, together with the observation that Liesegang rings may be formed in an aqueous medium (*e.g.*, solutions of calcium chloride and sodium carbonate), widen considerably the whole aspect of the Liesegang phenomenon and show definitely the inadequacy of any single theory, hitherto advanced, to afford a proper explanation.

The influence of light, studied by several investigators (Davies, *J. Amer. Chem. Soc.*, 1923, **45**, 2261; Tryhorn and Blacktin, *Trans. Faraday Soc.*, 1923, **19**, 433), is to a large extent accounted for by the photochemical changes it induces, but it also involves a milder and much more general effect, that of local activation, or formation of nuclei. Careful study of the tree formation showed that in more than 70% of the cases the direction of the spiral tended towards the illuminated side of the vessel no matter where the trees originated. After fully considering such disturbing factors as the sensitiveness of the trees to traffic-vibration, reflexion, and general difficulty of localising the light, the influence of light upon orientation can scarcely be doubted. This finds ready support in the fact that when sodium carbonate solution acted upon a set gelatin solution of calcium carbonate, the reaction taking place in a glass cylinder of 2·5 cm. diameter, the Liesegang rings were not horizontal, though parallel to one another. The rings seemed to incline invariably towards the illuminated side of the vessel, suggesting that diffusion, and therefore interaction, was more rapid on that side.*

EXPERIMENTAL.

Section I. (With George Ernest Wilson.)

Ring Formation with One Basic Salt.

Sodium Carbonate.—Series 1; 1% *solution.* Graduated test tubes (2 cm. × 15 cm.) containing a set solution of gelatin † (5—8 cm. in height) were almost filled with a 1% sodium carbonate solution and allowed to stand. At the salt–gelatin junction, a translucent concave membrane soon formed. On further standing, rings gradually appeared below this membrane, and examination showed them to be considerably thicker than the membrane. Under the magnifying glass, they were seen to consist of a multitude of fine globules, in the form of a gelatinous precipitate, the compactness of packing diminishing upwards. The inter-band distances progressively increased with each succeeding ring. After 7 days, 4 bands appeared, increasing to 6 at the end of 14 days. Measurements by means of a cathetometer gave the following figures: After 7 days, the membrane had moved down 0·2 cm., the curvature of meniscus was 0·1 cm., and the distances from the position of the membrane to the consecutive bands ‡ were 0·4, 0·8, 1·3, and 1·9 cm., respectively. After 14 days, the membrane had moved down 0·5 cm., the curvature was 0·25 cm., and the distances from the *new* position of the membrane to the consecutive bands were 0·7, 0·9, 1·4, 2·1, 2·8, and 3·5 cm., respectively.

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* Some years ago, the author made similar observations on the crystallisation of certain substances from solution. Mere evaporation would scarcely account for the invariable primary appearance of the crystals on the more illuminated side of the vessel. Davies (*loc. cit.*) found that light influenced ring formation in a medium of colloidal gold.

† In all the experiments "Gelatine extra" of Coignet Père, Fils, et Cie. was used, the solutions (usually 5%) being employed within 12 hours of their preparation. The experiments were carried out in a basement having a concrete floor, so as to eliminate as far as possible the effect of light and vibration.

‡ In all measurements, the edge of the membrane was taken as an indication of its position, as, owing to diffusion and osmotic pressure, the mem-

The number of bands formed after 7 and 14 days, given above, does not really indicate the rate of formation of bands, as the membrane in its movement downwards first depresses the bands and then absorbs them. But even after 3 months, when the diffusion was complete, the adhesion of the remains of the bands to the walls of the tube was sufficiently strong to leave a record of their original position.

Series 2; 5% *solution.* When experiments were carried out as in series 1, but with a 5% solution of sodium carbonate, the texture of the bands was more compact, and the inter-band spaces were comparatively smaller.

After 2 days, 7 bands had formed; membrane (concave) had moved down 0·5 cm. from original position; curvature of meniscus, 0·1 cm.; distances from membrane to consecutive bands were 0·6, 0·9, 1·2, 1·5, 2·0, 2·5, 3·1 cm., respectively.

After 7 days, 9 bands had formed; membrane had moved down 0·9 cm. from original position; curvature of meniscus, 0·4 cm.; distances of bands from new position of membrane, 1·0, 1·2, 1·5, 1·9, 2·4, 3·0, 3·7, 4·5, 5·4 cm., respectively, the bands reaching the bottom of the tube.

After 14 days, 8 bands remained; membrane had moved down 1·5 cm. from original position; curvature, 0·8 cm.; distances of bands from membrane, 1·0, 1·3, 1·6, 1·9, 2·4, 3·0, 3·7, 4·8 cm., respectively (see Fig. 1).

After 3 months, the membrane had moved down 2·4 cm.; the bands were very distinct, and composed of coarse, spherical granules in a clear space, the inter-band space being cloudy. After 6 months, the membrane had reached the bottom of the tube, leaving the remains of the bands adhering to the walls (as rings of cloudy gelatinous matter) on pouring out the solution.

Series 3; 10% *solution.* Formation of bands was similar to that in series 2, the bands being closer together and still more solid in texture. After 7 days, 7 bands had formed, and the concave meniscus of the membrane (curvature, 1·0 cm.) actually penetrated the first band. After 14 days, 10 bands were formed, and reached the bottom of the tube; membrane concave; curvature, 0·9 cm.

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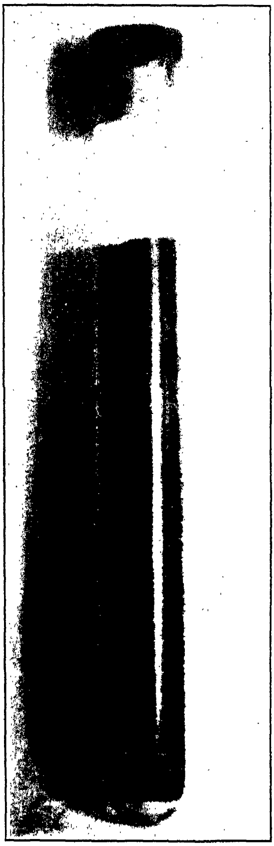
branes were in all cases convex or concave. (*Note.* A water–air meniscus is regarded as concave.)

In measuring the inter-band distances, the bottom of a band was taken, as this was quite definite, whilst the top was practically always diffuse.

Fig. 1.

Fig. 2.



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Series 4; 15% *solution.* Gradual formation of bands, 2 mm. in thickness, and inter-band distance gradually increasing from 1 mm. to 3 mm.

Series 5. *Concentric ring formation with sodium carbonate.* A crystal of sodium carbonate was allowed to penetrate the whole thickness of a set 5% gelatin solution contained in a Petri dish. Concentric rings were formed similar to the bands described above. The same effect was obtained by filling with sodium carbonate solution a cylindrical hole bored through the whole thickness of the gelatin. On the contrary, placing a drop of the sodium carbonate solution on the surface of the gelatin gave no definite rings, the horizontal diffusion not being simultaneous through the whole depth of the gelatin. No bands were obtained on substituting agar-agar for gelatin.

Sodium Hydrogen Carbonate.—The presence of sodium hydrogen carbonate exerted an inhibiting effect on ring formation. The salt itself showed but small tendency to stratification, the bands being few and imperfect.

Sodium Hydroxide (4% *solution*).—The membrane had a concave meniscus, and faint, imperfect bands were formed, a brownish gelatinous precipitate separating.

Barium Hydroxide.—*Series* 1; 3·5% *solution.* A flat membrane was formed at the junction of the barium hydroxide solution and the gelatin. After 7 days, a cloudy space of about 1 cm. below the membrane was observed, followed by a space of 1·4 cm. occupied by 10 fine rings. After 14 days, the membrane had moved down 2·5 cm., this space being occupied by 25—30 fine bands. Below the membrane a space of 5·0 cm. contained 17 bands. No further change was observed after 21 days.

Series 2; 7% *solution.* After 7 days, the flat membrane had moved down 2·0 cm. from its original position, and above it were very fine, close, film-like bands in two layers: (*a*) upper layer, about 40 equidistant bands occupying 1·8 cm.; and (*b*) lower layer, about 30 equidistant bands, occupying 2·0 cm. Below the membrane was a slightly cloudy region of 2·4 cm. containing 14 distinct bands.

After 14 days, the membrane had moved down 5·4 cm. from its original position, this space being occupied by about 60 bands, the inter-band space increasing from 0·3 mm. to 1·0 mm. towards the membrane. Below the membrane 6 bands were formed, occupying 2·1 cm.

After 21 days, the membrane had reached the bottom of the tube, and below the original position of the membrane the tube was filled with bands, gradually increasing in thickness and distance apart towards the bottom of the tube. After the contents of the tube had been poured out, the rings adhered to the walls as a white precipitate (see Fig. 2).

The peculiarity of the bands above the membrane, in so far as they differ in appearance and structure from those below, would simply show that they were formed after the passage of the membrane.

Series 3. *Agar-agar medium* (1%). (*a*) Barium hydroxide, 3·5%. A concave membrane was formed, moving down 0·2 cm. in 7 days. A heavy precipitate was found on the membrane, below which was a clearer space of 1·2 cm. followed by a thick band of a distinct yellow colour. Below this the gel was of a green tint.

(*b*) Barium hydroxide, 7·0%. Membrane had moved down 0·1 cm. in 7 days. A very heavy precipitate was on the membrane, below which was a clearer space of 0·3 cm. then one very thick band of yellow colour. Below this, the gel was green.

Ammonium Hydroxide.—Series 1; 5% *solution.* A convex membrane, moving up 1·1 cm. in 7 days, was formed at the junction of the 5% solutions of ammonia and gelatin. This membrane had a rough surface, composed of feathery particles. No bands were observed. After 3 months, the membrane had moved up 5·8 cm., having become flat and indistinct. One band, composed of coarse particles, had appeared 0·3 cm. below the new membrane. The rest of the gel was cloudy. With ammonia solution (*d* 0·880), the diffusion was similar but slower.

Series 2. *Ammonia gas.* Test tubes containing set 5% gelatin solution were filled with ammonia gas and allowed to stand hermetically closed. The gelatin solution liquefied.

Series 3. *Gaseous ammonia–nitrogen mixture.* A 100 c.c. measuring cylinder, containing 75 c.c. of 5% set gelatin solution, was connected to a nitrometer containing a mixture of ammonia gas and nitrogen in the ratio 1 : 3. After 30 minutes, a cloudy membrane was formed, complete liquefaction occurring within 24 hours; the column of liquid presented the appearance of opacity bands, extending throughout the liquid, the band thickness and inter-band distances (equal) being 2·4 cm. (approx.). The opacity bands gradually disappeared, nothing except a general turbidity remaining after 3 hours. On increasing the proportion of ammonia, ordinary liquefaction occurred as in series 2.

Calcium Hydroxide (*Saturated solution*).—A transparent, convex membrane was formed, moving up 0·3 cm. in 14 days. Below the membrane was a cloudy region of 3·2 cm. containing 2 broad bands.

Ring Formation with One Acid.

Series 1; 5% *solution of hydrochloric acid.* A concave membrane composed of fine particles was formed, moving down 3·6 cm. in 7 days. Above the membrane was a cloudy region. As the membrane moved down, faint bands were formed below it. After 3 months, diffusion was complete, the liquid being cloudy. In contrast to those with sodium carbonate, the bands were only of a temporary nature, gradually disappearing. Weaker acid solutions gave no definite bands.

Series 2; 10% *solution.* A concave membrane was formed, moving downwards. After 5 days, very fine translucent bands were formed, slightly resembling the sodium carbonate bands, but farther apart. After 3 months, the diffusion was complete and a white precipitate was at the bottom of the tube. Using 15% and 32% hydrochloric acid, and hydrogen chloride gas (as in the case of ammonia gas) neither membrane nor bands were formed, diffusion increasing with strength of acid.

Experiments with a series of other acids, both organic and inorganic, and also with single salts were carried out, but no definite ring formation was observed. It is noteworthy that, in the majority of cases, inorganic acids gave a concave meniscus moving downwards, whilst organic acids gave a convex one moving upwards.

Bromine Water (*saturated*).—A flat membrane was formed, below which was a thick, opaque mass, followed by a cloudy region. After 11 days, the membrane had moved up 0·8 cm. with an opaque region of 2·1 cm. beneath, and then 2 bands in a cloudy space.

Silver Nitrate (1·7% *solution*).—*In the light.* In place of the ordinary membrane, a dark, wide band was formed. 0·3 Cm. below the first band another wide, dark band was formed, followed by about 2 cm. clear space, and then well-defined bands similar to those in the sodium carbonate experiments.

After 3 months, the membrane band was deep red, and stationary. At the bottom of the tube were 6 distinct bands, 7·6 cm. from the membrane band. A grey deposit on the tube, forming a mirror in places, was seen above the membrane band.

In the dark. Concave membrane.

No bands formed at first. After 14 days, the membrane was still stationary; below it were a dark brown region of 1 cm. and, at the bottom of the tube, faint bands (5 bands in 2·1 cm.).

After 3 months, the membrane was solid and red. The solution was reddish-brown, and the gel red; 7 distinct bands were at the bottom of the tube, 7·0 cm. from the membrane, the intermediate space being clear. No mirror.

No bands were observed on substituting agar-agar for gelatin.

Silver Nitrate and Formaldehyde (0·5% Solution of silver nitrate in 5% gelatin solution, and 40% formaldehyde above).—*In the light.* Membrane reddish-brown, steeply concave, opaque, and 0·2 cm. thick. Beneath the membrane a clear space of 3 cm. with one band. Gelatin below slightly opaque, and reddish-brown.

After 3 months, membrane was steeply concave (0·8 cm.) and 3 bands were seen in the gel, taking the same shape as the membrane.

In the dark. Membrane white, opaque, steeply concave, and 0·1 cm. thick.

Above the membrane was a cloudy layer about 1 cm. thick. No bands of clear space.

After 3 months, the gel was dark brown. No bands or mirror.

Formaldehyde (40% *solution*).—A hard, horny, concave membrane was formed, still stationary after 3 months. The appearance of the gelatin remained unchanged, but on careful examination it was found that its consistency had altered completely, having become hardened throughout in layers. Under the pressure of a glass rod, the layers could easily be distinguished as separated by clear, hard membranes. The gelatinous mass bore a remarkable resemblance to the crystalline lens of an eye. The formaldehyde solution became weaker. Similar results were obtained by employing the 20% solution.

No optical examination could be made of this interesting experiment.

Similar experiments with absolute ethyl alcohol or acetone resulted in the formation of slightly concave, parchment-like, non-permeable membranes. No change was observed after 3 months' keeping.

Section II. (With HUBERT CAWOOD HILLARY and HOWARD BRAITHWAITE STENT.)

Calcium Carbonate and the Liesegang Phenomenon.

As already indicated (J., 1923, **123**, 785), the formation of hydrocalcite ($CaCO_3,5H_2O$) was brought about by forced double decomposition *en masse* of calcium chloride and sodium carbonate. On the other hand, when the interaction was allowed to take a more natural course (*i.e.*, the velocity of reaction was dependent on the rate of diffusion), a series of new and interesting phenomena were observed. To prevent the reaction being instantaneous, advantage was taken of the fact that concentrated solutions of calcium chloride and sodium carbonate differ widely in specific gravity.

On carefully running 600 c.c. of 7% solution of pure sodium carbonate on to 200 c.c. of a 38% solution of pure calcium chloride contained in a 1000 c.c. glass cylinder, both solutions being at room temperature, a gelatinous semipermeable membrane of hydrocalcite was formed. After 2 hours, the membrane had increased in thickness, the bottom part of the calcium carbonate (the original membrane) showing distinct signs of changing from the translucent gelatinous (hydrocalcite gel) condition to an opaque white crystalline solid (calcite). After 4—5 hours, the membrane had increased in opacity and thickness, showing the solid to be uniformly distributed asbestos-like layers, which in the course of 2 or 3 days spread to a depth of 1·2 cm. Simultaneously with the hardening of the membrane, one or more protuberances or hillocks were observed on the upper layer of the solid. The hillocks soon resembled miniature volcanoes, the eruptions taking the form of fine streamers extending nearly to the surface of the liquid in straight, though not always vertical, chains of gelatinous particles of calcium carbonate. The shot-out streamers, on reaching the surface of the liquid, appeared to bend over and then gradually vanish, giving rise to the remarkable phenomenon of opacity bands or rings, distributed uniformly throughout the upper part of the sodium carbonate solution. In place of the streamers trees began to grow, taking their origin from the protuberances. The trees had the appearance of a wavy, white line or column in a spiral form, the corrugated surface of the column recalling stalagmites or icicles. Not infrequently, the trees were imperfect in their spiral form, being confined almost to one plane. In these cases, the wave maxima invariably coincided with the opacity bands.

After 12—20 hours, the trees extended to the surface of the liquid, often creeping along the walls of the vessel. On nearly reaching the surface, the trees spread into a growth resembling sea plants. This foliage, or calcium carbonate in layers, gradually fell on to the membrane, carrying with it some of the trees, and completely destroying the opacity regions, already disturbed by the growth of the trees. The phenomenon of layers and tree formation persisted apparently indefinitely, provided that experimental conditions remained constant. The trunks of the trees were found to be hollow, a horizontal section of the walls showing concentric rings when magnified.

On long keeping, the bottom part of the laminar membrane gradually broke up and fell to the bottom of the vessel in the form of a fine, crystalline powder of calcite. The edges of the remaining opaque and hardened layers assumed in course of time a zig-zag shape. No appreciable difference was caused by varying the diameter of the vessel or the height of the columns of solution.

On diminishing the concentration of the sodium carbonate, the whole phenomenon of ring and tree formation became fainter. Reduction of the concentration of the calcium chloride solution, *i.e.*, bringing its specific gravity nearer to that of the sodium carbonate solution, prevented the formation of a membrane and resulted in rapid diffusion.

Experiments were carried out with sodium carbonate and calcium chloride in (*a*) tap water, (*b*) distilled water, (*c*) boiled solution cooled under reduced pressure, (*d*) in the dark, and (*e*) in sunlight; the actual tree growth was unaffected by these modifications of conditions.

Influence of Temperature.—On carrying out the experiments at 0—3°, no tree formation took place, so long as the membrane remained gelatinous. Only on the transformation of the gelatinous membrane (hydrocalcite) to the opaque crystalline layers (calcite), did it become impermeable to diffusion, the force of osmosis breaking through at one or more places of least resistance, forming protuberances, and finally trees. But even at low temperatures some streamers were formed, giving rise to well-defined opacity bands, having a spacing of approximately 0·9 cm. and being ultimately destroyed by the tree formation, on raising the temperature. Above 30°, no Liesegang rings or trees were formed, owing to rapid diffusion and to the fact that at this temperature hydrated calcium carbonate has not even a temporary existence. The semipermeable character of the membrane was well illustrated by colouring the sodium carbonate solution with phenolphthalein or potassium permanganate. In each case, no coloration could be observed below the membrane. Similar results were obtained by colouring the calcium chloride with potassium permanganate.

Calcium Chloride, Sodium Carbonate, and a Colloid.

A narrow 100 c.c. cylinder was half-filled with a 5% solution of gelatin containing 3 g. of calcium chloride per 100 g. of gel. When the gel had set, 50 c.c. of a 15% solution of sodium carbonate were slowly poured on. A whitish membrane was formed, and slow diffusion took place into the gel, causing it to become opalescent. The upper solution remained clear. After 60 hours, the diffusion was complete, the white bands being separated by opalescent spaces speckled with calcium carbonate.

A 1% gel of agar-agar in distilled water, containing 2% of sodium carbonate, with a superimposed 10% solution of calcium chloride gave precipitation of a rhythmic character. With 3% of calcium chloride in the agar-agar gel and 10% sodium carbonate solution above, the precipitation was uniform and slow.

In all cases where gelatin or agar-agar was employed, no streamers, trees, or opacity bands were observed, the reason probably being that the transition point hydrated—anhydrous calcium carbonate is considerably raised in presence of colloids (compare mother-of-pearl).

Well-defined concentric rings were obtained by fixing a crystal of sodium carbonate in a Petri dish containing set 5% gelatin, with 3% of calcium chloride in solution. The development of the rings was very similar to that described in the case of sodium carbonate (see Section I).

Influence of Light.—As already stated, the access of light influenced the direction of both the trees and the calcium carbonate rings in the gelatin medium. In the experiments on the effect of light on the tree-orientation, vessels 10—13 cm. in diameter were employed. These were entirely covered with black paper, a narrow slit being allowed to remain on the side facing the light. Sunlight, electric and gas lights were tested, the most satisfactory result being given by sunlight. When precautions were taken to prevent vibration and to keep conditions constant, in more than 70% of the cases the trees tended towards the light, regardless of the position of the protuberances. No such relationship could be observed in the case of streamers.

Interesting results were obtained by using vessels (of diameters varying from 3—12 cm.) enclosed in black paper in which small circular apertures were made at various heights of the sodium carbonate column. The light was admitted through a lens, thus focussing it at any particular point in the vessel. It was invariably found that the trees tended towards the focus, so much so that often several of them met in a point, becoming entangled.

In the experiments with a gelatin medium carried out (*a*) in complete darkness, (*b*) in the light, and (*c*) in a vessel covered with black paper, the light being admitted through a narrow slit, the only difference observed between (*a*) and (*b*) was in the velocity of diffusion, the rings being horizontal and equally spaced; in the case of (*c*), the rings, whilst remaining parallel to one another, were inclined towards the light.

Influence of Hydroxy-compounds upon the Colloidal Condition of Calcium Carbonate.—A series of experiments was carried out on lines similar to those described by Neuberg and Rewald (*Biochem. Z.*, 1908, 9, 547). Both calcium oxide and calcium metal, suspended in absolute ethyl or methyl alcohol, glycerol,* or mixtures of these, gave colloidal calcium carbonate in presence of carbon dioxide. The stability, viscosity, and concentration of the resulting product depended upon the medium and experimental conditions.

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* Colloidal calcium carbonate in glycerol may be of therapeutic interest.

Influence of Gelatin upon the Colloidal Condition of Calcium Carbonate.—10 G. of powdered lime were suspended in 200 c.c. of hot 5% gelatin solution. A current of carbon dioxide was passed through for 5 hours, the temperature being allowed to drop to 25°. On keeping, the gelatin solution set to a brownish, opalescent gel, the excess of lime remaining caked at the bottom of the vessel. A white precipitate was thrown down on shaking the gel with water, methyl alcohol, or acetone. Analysis showed the gel to contain 0·67% of calcium carbonate.

No definite results were obtained with agar-agar.

Summary.

(1) The Liesegang phenomenon is a material record of a periodic function, *viz.*, the action of a single substance upon a mobile medium, capable of undergoing either structural deformation or systematic orientation. Such a medium may be a colloid or finely-divided suspended matter. The substance is, as a rule, sufficiently strongly acidic or basic to cause a physical change in the medium. The suitable character of the substance and the condition of the medium may be developed *in situ.*

(2) Opacity bands and tree formation are special cases of the Liesegang phenomenon, the former being produced under very mild experimental conditions, and the latter under the influence of forced irregular diffusion.

THE UNIVERSITY, MANCHESTER. [*Received, September* 11*th*, 1924.]

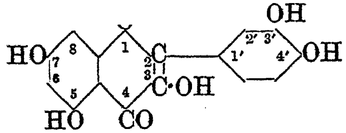
XXXVI.—*The Position of the Sugar Nucleus in the Quercetin Glucosides.*

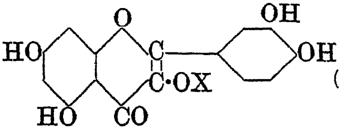
By GORDON FREDERICK ATTREE and ARTHUR GEORGE PERKIN.

A KNOWLEDGE of the position of the sugar nucleus in the flavonol glucosides is of special interest, on account of the inter-relationship between these compounds and the naturally occurring anthocyanins. From an examination of the dyeing properties of the hydroxy-flavone and -flavonol colouring matters, especially towards aluminium and tin mordants, it has been possible to estimate the tinctorial effect of each of the hydroxyls present in these compounds and thus to predict to some extent the position of the sugar nucleus in their glucosides.

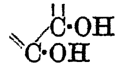
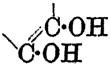
It is now known in regard to quercetin (I) that three factors influence its dyeing property in this respect: (*a*) the hydroxyls 5 and 7, the effect of which is almost negligible (pale yellow); (*b*) the hydroxyls 3′ and 4′, which jointly are powerful auxochromes (deep yellow); and (*c*) the hydroxyl 3, which itself creates dyeing property (pale yellow) and enhances that given by (*b*) to deep orange.

(I.)



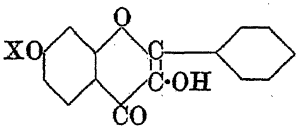


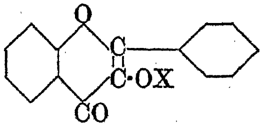
(II.)

Interesting again is the fact that the pale yellow shade due to hydroxyl 3 is much strengthened by the presence of hydroxyl 7 or 4′, and if *p*-quinonoid formulæ are adopted, this effect may be assumed to originate in the group  or  present.

Mainly from these considerations, it was predicted (J., 1899, **75**, 826; 1902, **81**, 589) that as quercitrin gives yellow tones, the rhamnose nucleus present therein will be in union with either the 3- or the 3′-hydroxyl group, and of these, the former suggestion (II) is now known to be correct. Thus, by the action of diazomethane on quercitrin, Herzig and Schönbach (*Monatsh.*, 1912, **33**, 678) obtained a crude quercitrin pentamethyl ether, which when hydrolysed gave the 5 : 7 : 3′ : 4′-tetramethoxyflavonol previously synthesised by v. Kostanecki, Lampe, and Tambor (*Ber.*, 1904, **37**, 1402), thus indicating that the rhamnose nucleus is present in the 3-position. More recently, Shibata and Kimotsuki (*Acta Phytochim*, 1923, **1**, 91) have studied the ultra-violet absorption spectra of hydroxy-flavones and -flavonols, and find that by this method it is possible to distinguish the one from the other. Tasaki (*ibid.*, 1925, **2**, 129) has similarly examined the hydroxy-flavone and -flavonol glucosides and as a result considers that these fall into the groups (III) and (IV) in regard to the position of the sugar group (X) present.

(III.)





(IV.)

In group (III) occur the flavone glucosides, and rutin, whereas in group (IV) are placed the flavonol compounds, robinin, kæmpferitrin, quercitrin, and myricitrin. Such a formulation (IV) is in full agreement with the dyeing properties of the latter, and is certainly correct in regard to quercitrin (*loc. cit.*).

On the other hand, the inclusion of the quercetin glucoside rutin in group (III) does not harmonise with the tinctorial behaviour of this compound.

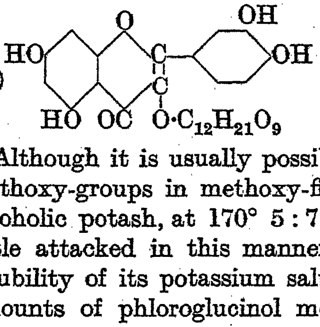
The experiments herein described are concerned with the methylation of rutin, xanthorhamnin, *iso*quercitrin, and quercimeritrin with diazomethane, and have clearly indicated the position of the sugar group in these glucosides.

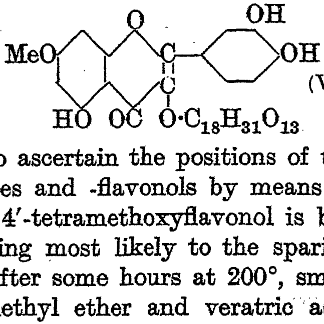
The rutin employed was obtained from the leaves of the *Eucalyptus macrorhyncha* (Smith, J., 1898, **73**, 697; Perkin, J., 1902, **81**, 478) and yielded with diazomethane a dull orange resin, $C_{27}H_{25}O_{11}(OMe)_5$.

Although ter Meulen (*Rec. trav. chim.*, 1923, **42**, 280) has stated that rutin is $C_{33}H_{42}O_{20},4H_2O$ and is derived from quercetin and the trisaccharide rhamninose, Charaux (*Compt. rend.*, 1924, **178**, 1312) finds that the older formula $C_{27}H_{30}O_{16}$ is in reality correct and that the sugar group present therein is the disaccharide rutinose.

When hydrolysed with dilute acid, rutin pentamethyl ether gave 5 : 7 : 3′ : 4′-tetramethoxyflavonol, the identity of which was confirmed by comparison with a specimen derived from quercitrin according to the directions of Herzig and Schönbach (*loc. cit.*). Rutin thus possesses the formula (V), and the statement of Tasaki that the sugar nucleus of this glucoside is present in the 7-position is therefore incorrect.

(V.)





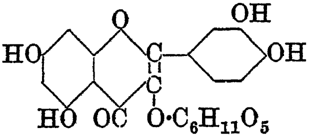
(VI.)

Although it is usually possible to ascertain the positions of the methoxy-groups in methoxy-flavones and -flavonols by means of alcoholic potash, at 170° 5 : 7 : 3′ : 4′-tetramethoxyflavonol is but little attacked in this manner, owing most likely to the sparing solubility of its potassium salt. After some hours at 200°, small amounts of phloroglucinol monomethyl ether and veratric acid were produced, but the presence of phloroglucinol dimethyl ether could not be detected. It is thus probable that at the high temperature involved, a preliminary conversion of the 5 : 7 : 3′ : 4′-tetramethoxyflavonol into the 5-hydroxy-7 : 3′ : 4′-trimethoxy-compound takes place, and that this then suffers hydrolysis as indicated above.

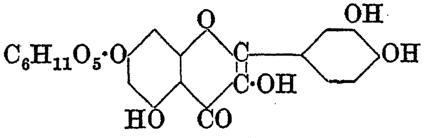
Xanthorhamnin, $C_{34}H_{42}O_{20}$, a yellow-dyeing glucoside obtained from Persian berries, consists of rhamnetin (quercetin 3-monomethyl ether) in union with the trisaccharide rhamninose (Tanret, *Compt. rend.*, 1899, **129**, 725). This, with excess of diazomethane, gave a yellowish-brown resin, which by hydrolysis with acid yielded similarly to quercitrin and rutin the 5 : 7 : 3′ : 4′-tetramethoxy-flavonol. Xanthorhamnin thus has the structure (VI). When less diazomethane is employed, a methylation product can be isolated as pale yellow needles, which approximates in composition to a xanthorhamnin trimethyl ether, $C_{34}H_{39}O_{17}(OMe)_3,3H_2O$. Hydrolysis gave yellow needles consisting mainly of a quercetin trimethyl ether, evidently the 7 : 3′ : 4′-compound, but containing a trace of the 5 : 7 : 3′ : 4′-tetramethoxyflavonol.

iso*Quercitrin*, $C_{21}H_{20}O_{10}$, which consists of quercetin in union with glucose, is present in cotton flowers (Perkin, J., 1909, **95**, 2190) and in brown husked maize (Sando and Bartlett, *J. Biol. Chem.*, 1922, **54**, 636).

The small amount available gave with diazomethane pale yellow, flat needles of a methylated glucoside, m. p. 150—152°, and from this by hydrolysis 5 : 7 : 3′ : 4′-tetramethoxyflavonol was produced. *iso*Quercitrin (VII) is thus analogous to rutin and xanthorhamnin.



(VII.)



(VIII.)

Quercimeritrin, $C_{21}H_{20}O_{12}$, occurs in cotton flowers (Perkin, *loc. cit.*), in *Prunus emarginata* (Finnemore, *Pharm. J.*, 1910, **31**, 604), and in *Helianthus annuus* (Sando, *J. Biol. Chem.*, 1925, **64**, 74).

It differs from the yellow-dyeing *iso*quercitrin in giving orange shades similar to those obtained from quercetin itself, and mainly on this account was considered most probably to possess the formula (VIII) (Perkin, *loc. cit.*). With diazomethane, it gave almost colourless needles, m. p. 203—205°, sintering at 197°, which there is little doubt consist of the pentamethyl ether, $C_{21}H_{15}O_7(OMe)_5,2H_2O$. By hydrolysis, colourless needles of a sparingly soluble quercetin tetramethyl ether, m. p. 284—285°, were obtained, the acetyl derivative of which melts at 174—176°. As this, when digested with alcoholic potash at 180°, readily gives veratric acid and phloroglucinol monomethyl ether, it is evidently the hitherto unknown 5 : 3 : 3′ : 4′-tetramethoxy-compound. Thus of the five possible quercetin tetramethyl ethers, three only can give veratric acid. These are now known, and as the 7 : 3 : 3′ : 4′- and the 5 : 7 : 3′ : 4′-compounds melt respectively at 156—157° and 195—198°, the quercetin tetramethyl ether derived from quercimeritrin must possess the constitution here stated. Quercimeritrin therefore has the formula (VIII), which, as already suggested, is in harmony with its dyeing properties.

Of the five known quercetin glucosides, therefore, four contain the sugar group in union with the pyrone hydroxyl, and if, as appears likely (compare Tasaki), kæmpferitrin, robinin, and myricitrin are analogously constituted, quercimeritrin will be the only known flavonol glucoside which differs in this respect.

EXPERIMENTAL.

Rutin (2 g.) in methyl alcohol (30 c.c.) was treated with diazomethane prepared from nitrosomethylurethane (8 c.c.) in ether (80 c.c.) and 25% methyl-alcoholic potash (25 c.c.); precipitation of the rutin by the ether was prevented by additions of methyl alcohol (5 c.c.) from time to time (compare Herzig and Schönbach, *loc. cit.*). On the following day, the solution was again treated as before with diazomethane; then, after 48 hours, it was concentrated, diluted with boiling water to remove the last traces of alcohol, and evaporated to dryness (Found: CH_3, 11·4. Rutin pentamethyl ether, $C_{32}H_{40}O_{16}$, requires CH_3, 11·0%). The yellowish-brown resin was digested with boiling 0·5% sulphuric acid (200 c.c.) for 2 hours, yielding a precipitate which crystallised from benzene in colourless needles; these, alone or mixed with 5 : 7 : 3′ : 4′-tetramethoxyflavonol prepared from quercitrin by Herzig and Schönbach's method, melted at 194—196° (Found: C, 63·6; H, 5·1; CH_3, 16·5. Calc. for $C_{19}H_{18}O_7$: C, 63·7; H, 5·1; CH_3, 16·75%). The acetyl derivative melted at 160—162° (Herzig and Schönbach give m. p. 160—163°).

Xanthorhamnin (2 g.) in methyl alcohol (50 c.c.) was treated with diazomethane as in the case of rutin; after being kept over-night, the liquid, containing crystals in suspension (A), was evaporated to half its volume, and again treated with diazomethane from nitrosomethylurethane (4 c.c.). The solution was evaporated to dryness and the residue digested with boiling 0·5% sulphuric acid (100 c.c.). The precipitate obtained crystallised from benzene in colourless needles, m. p. 194—196°, and, admixed with the 5 : 7 : 3′ : 4′-tetramethoxyflavonol derived from rutin, showed no alteration in melting point.

If the mixture (A) was evaporated to half its volume and kept, fine, colourless needles (1·7 g.) separated. These melted at 175—178° (those from a second experiment at 172—178°), became yellow when dried over sulphuric acid, were readily soluble in water, and gave with ferric chloride a brown coloration (Found: H_2O at 140°, 6·7; CH_3, 6·8. Xanthorhamnin trimethyl ether, $C_{37}H_{48}O_{20},3H_2O$, requires H_2O, 6·2; CH_3, 6·8%). On hydrolysis with boiling 1% sulphuric acid, fine, yellow needles separated which, after recrystallisation from alcohol, melted at 170—172° (Found: CH_3, 14·1. $C_{18}H_{16}O_7$ requires CH_3, 13·1%). It was evidently quercetin 7 : 3′ : 4′-trimethyl ether (rhamnetin dimethyl ether) contaminated with a small amount of the 5 : 7 : 3′ : 4′-tetramethoxy-compound.

iso*Quercitrin* (0·6 g.) in methyl alcohol was treated with diazomethane from nitrosomethylurethane (4 c.c.); crystals separated over-night. The ether was distilled off, and the liquid again treated with diazomethane as before. Pale yellow needles slowly separated (0·4 g.) which sintered slightly at 140° and melted at 150—152°. This compound, on hydrolysis with boiling 1% sulphuric acid, gave needles which, after recrystallisation from benzene, melted at 193—195°, and, as a mixed melting-point determination showed, consisted of 5 : 7 : 3′ : 4′-tetramethoxyflavonol.

Quercimeritrin (2 g.) in methyl alcohol (80 c.c.) was methylated with ethereal diazomethane from nitrosomethylurethane (8 c.c.), methyl alcohol (20 c.c.) being added gradually at the same time. On the following day, the ether was removed by distillation, methyl alcohol (50 c.c.) added, and the solution again treated with the same amount of diazomethane. When the latter proved to be absent, the liquid was evaporated to a small bulk and diluted with a few drops of water; almost colourless needles (1 g.) then slowly separated. These sintered at 197°, melted at 203—205°, and could be recrystallised from water. With ferric chloride solution, no coloration was produced, indicating complete methylation (Found:* C, 54·05; H, 6·0; H_2O, 6·7. $C_{26}H_{30}O_{12},2H_2O$ requires C, 54·7; H, 6·0; H_2O, 6·3%). This compound, apparently quercimeritrin pentamethyl ether, on hydrolysis (1 g.) with boiling 1% sulphuric acid for 4 hours, gave a semi-gelatinous precipitate (0·635 g.). It was dissolved in much boiling alcohol in presence of animal charcoal, and the solution evaporated until crystallisation commenced. The fine, colourless needles obtained were evidently pure, as the melting point, 284—285°, was unaltered after recrystallisation (Found:* C, 63·6; H, 5·1. $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%).

This new *quercetin tetramethyl ether*, which is very sparingly soluble in alcohol, dissolves in alkaline solutions with a pale yellow colour. The *acetyl* derivative forms minute, colourless needles, m. p. 174—176° (Found:* C, 62·8; H, 5·3; CH_3, 14·2. $C_{21}H_{20}O_8$ requires C, 63·0; H, 5·0; CH_3, 15·0%). In order to determine the positions of the methoxy-groups, the tetramethyl ether (0·6 g.) in 20% alcoholic potash (5 c.c.) and water (1 c.c.) was heated at 170—180° for 3 hours. The pale yellow liquid was evaporated to dryness, the residue dissolved in water, and the solution saturated with carbon dioxide. Extraction with ether removed a colourless, viscid product, the solution of which in dilute aqueous sodium carbonate was treated with benzenediazonium chloride. The orange-red precipitate was dried and extracted with a little alcohol, and the residue was crystallised from alcohol–acetic acid. The crystals, m. p. 250—252°, evidently consisted of benzeneazophloroglucinol monomethyl ether. Addition of acid to the bicarbonate solution remaining after the extraction with ether gave a deposit of veratric acid, m. p. 174—176°. The quercetin methyl ether, m. p. 284—285°, derived, as above stated, from quercimeritrin, is accordingly 5 : 3 : 3′ : 4′-tetramethoxyflavonol.

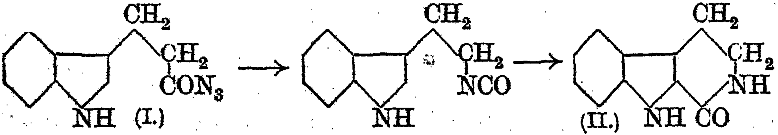
We are greatly indebted to Mr. Arthur Bennett of the Chemistry Department of the University of Manchester for the numerous microanalyses (marked*) which he has carried out in connexion with this work, and we desire to acknowledge a grant from the Department of Scientific and Industrial Research which enabled one of us (G. F. A.) to take part in this investigation.

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, November 29th, 1926.*]

XXXVII.—*The Decomposition of β-3-Indolylpropionic Azide.*

By RICHARD HELMUTH FRED MANSKE and ROBERT ROBINSON.

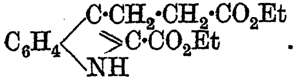
IN a recent synthesis of harmaline (Manske, Perkin, and Robinson, this vol., p. 1) advantage was taken of the Japp-Klingemann reaction for the preparation of arylhydrazones of certain α-diketones and α-keto-acids. In continuation of the work, an attempt was made to obtain 3-β-aminoethylindole by applying the Curtius reaction to β-3-indolylpropionic acid. A remarkably satisfactory method of preparation of this acid was devised, but the same process has quite recently (*Ber.*, 1926, **59**, 1858) been placed on record by Kalb, Schweitzer, and Schimpf, so that a detailed description is unnecessary; the chief variations are mentioned in the experimental section. Methyl β-3-indolylpropionate was converted in the normal manner into the related hydrazide and azide (I). The nature of the products obtained on the decomposition of the latter substance varies with the conditions, and in benzene solution, in presence of hydrogen chloride, the carbimide, which is doubtless initially formed, undergoes intramolecular condensation with the formation of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (II). The constitution of the product is proved by the fact that on distillation with zinc dust in a stream of hydrogen



it gives a small amount of norharman along with indole. The reaction involved is analogous to that occurring in the formation of *iso*quinoline by dehydration of cinnamaldoxime.

EXPERIMENTAL.

Ethyl β-2-*Carbethoxy*-3-*indolylpropionate*,



$$C_6H_4\left\langle\begin{matrix}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et \\ \gg C{\cdot}CO_2Et \\ NH\end{matrix}\right. .$$

—The following process gives excellent results, but it is essential to avoid needless delays. A benzenediazonium chloride solution is prepared from aniline (38 g.), concentrated hydrochloric acid (100 c.c.), sodium nitrite (28 g.), and ice (200 g.); potassium hydroxide (48 g.) is dissolved in water (600 c.c.). One-half of the latter solution is shaken in a separator with ethyl *cyclo*pentanonecarboxylate (63 g.) and a small volume of undissolved oil is taken up in benzene. The aqueous layer is added to crushed ice (400 g.), and the benzene layer shaken with the remainder of the alkali. About half the diazo-solution is then added to the solution of the ester and after a minute the remainder of the alkali is introduced from the tap funnel, followed by the second half of the diazo-solution. After 5 minutes, the solution is acidified with concentrated hydrochloric acid (100 c.c.) and the precipitated mass is washed by decantation and dried. This crude phenylhydrazone of ethyl hydrogen α-ketoadipate (55·6 g.) is refluxed with 98% alcohol (156 c.c.) and concentrated sulphuric acid (40 g.) for 2·5 hours. On addition of water, cooling, and washing with sodium hydrogen carbonate solution, the product is obtained in a granular form. It is dried and purified by distillation in a high vacuum; b. p. 212°/2 mm. (yield, 43 g.; m. p. 94°). The ester crystallises from benzene in large, colourless prisms, m. p. 95—96°. The results of elementary analysis of this ester, the dicarboxylic acid obtained on hydrolysis, and the indolepropionic acid derived by heating the dibasic acid were in satisfactory agreement with theory. *Methyl* β-3-*indolylpropionate* crystallises from methyl alcohol in prisms, m. p. 79—80° (Found: N, 7·1. $C_{12}H_{13}O_2N$ requires N, 6·9%).

β-3-*Indolylpropionhydrazide*, $C_6H_4{:}C_2H_2N{\cdot}C_2H_4{\cdot}CO{\cdot}N_2H_3$, was prepared by the interaction of the methyl ester (40 g.) and hydrazine hydrate (15 g.) (oil-bath at 140°); the product (yield, 39 g.) crystallised from alcohol in colourless, hexagonal prisms or tablets, m. p. 129—130° (Found: N, 19·9, 20·4. $C_{11}H_{13}ON_3$ requires N, 20·8%). This hydrazide is sparingly soluble in cold alcohol and moderately readily soluble in hot water.

3-*Keto*-3 : 4 : 5 : 6-*tetrahydro*-4-*carboline* (II).—Crushed ice (200 g.) was added to a solution of β-3-indolylpropionhydrazide (10 g.) in acetic acid (50 c.c.), and sodium nitrite (4 g.) dissolved in a little water was then introduced. The liquid became milky, and in a few minutes pasty, owing to the separation of the crystalline azide (I). This was collected, washed with water, and drained as far as possible; it was then gradually added to boiling benzene (75 c.c.). Nitrogen was evolved and when this stage was completed a stream of hydrogen chloride was led through the hot solution. The benzene was finally distilled, and the residue washed with dilute hydrochloric acid. The substance (yield, 6—7 g.) crystallises from alcohol (charcoal) in characteristic, colourless, spear-head-shaped, microscopic prisms, m. p. 173—174° (Found: C, 71·1; H, 5·4; N, 15·1. $C_{11}H_{10}ON_2$ requires C, 70·9; H, 5·4; N, 15·0%). This cyclic amide is sparingly soluble in cold alcohol or ether and is readily soluble in hot alcohol. It dissolves in warm concentrated hydrochloric acid, but is precipitated on the addition of water; no indole colour reactions are exhibited. On distillation with zinc dust in a stream of hydrogen the chief product was a neutral compound having the properties of indole, but by extraction of the distillate with dilute hydrochloric acid a small quantity of norharman was obtained. The base was recognised by its appearance and m. p. (198°), and by the blue fluorescence of its aqueous acid solutions.

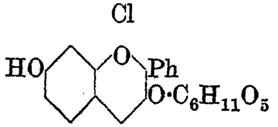
THE UNIVERSITY, MANCHESTER. [*Received, December 10th*, 1926.]

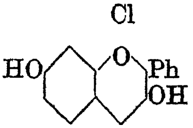
XXXVIII.—*Experiments on the Synthesis of Anthocyanins. Part II. The Synthesis of* 3- *and* 7-*Glucosidoxyflavylium Salts.*

By ALEXANDER ROBERTSON and ROBERT ROBINSON.

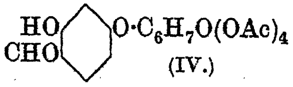
IN the first part of this series (J., 1926, 1713) it was shown that certain glucosides of pyrylium salts of anthocyanidin type may be prepared by relatively simple applications of the general method. In these cases, however, the carbohydrate group was associated with the position 4′ in the flavylium nucleus, whereas in the natural anthocyanins the available evidence shows that the sugar is attached to one of the positions 3, 5, and 7. Thus Willstätter and his collaborators found that all the anthocyanins derived from cyanidin gave a strong ferric chloride reaction and hence bear hydroxyl groups in positions 3′ and 4′. We have accordingly carried our investigation to a further stage by applying the processes already developed to the synthesis of flavylium salt glucosides which should, in respect of the position of the glucose residues, be more closely allied to the anthocyanins than any as yet obtained. ω-O-*Tetra-acetylglucosidoxyacetophenone*, $Ph{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}C_6H_7O(OAc)_4$ (I), prepared from benzoylcarbinol and tetra-acetylglucosidyl bromide with the help of silver carbonate, condensed with β-resorcylaldehyde in ethereal solution in presence of hydrogen chloride to a product which was not crystallised but was at once hydrolysed by means of methyl-alcoholic ammonia. The recovered pyrylium salt was difficult to purify, but, ultimately, 3-β-*glucosidoxy*-7-*hydroxyflavylium chloride* (II) was isolated. On hydrolysis, this yielded glucose and 3 : 7-dihydroxyflavylium chloride (III), which has also been obtained by a direct condensation of β-resorcylaldehyde and benzoylcarbinol, or its acetate. The salt has been previously obtained by demethylation of its 3-methyl ether (Pratt and Robinson, J., 1924, **125**, 191).

(II.)

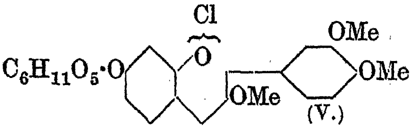




(III.)



(IV.)



(V.)

Similarly, the *tetra-acetylglucoside* (IV) has been prepared by the interaction of β-resorcylaldehyde and tetra-acetylglucosidyl bromide in acetone solution in presence of aqueous potassium hydroxide; in this case, condensation with ω-methoxyacetoveratrone was effected. The resulting flavylium chloride was deacetylated in the usual manner and 7-*glucosidoxy*-3 : 3′ : 4′-*trimethoxyflavylium chloride* (V) was then isolated in a satisfactory condition of purity. On boiling with hydrochloric acid, the glucose was detached and fisetinidin chloride trimethyl ether (Pratt and Robinson, J., 1925, **127**, 170) was obtained.

EXPERIMENTAL.

ω-O-*Tetra-acetyl*-β-*glucosidoxyacetophenone* (I).—Freshly-precipitated silver carbonate (6 g.) was added to a solution of *O*-tetra-acetyl-α-glucosidyl bromide * (6 g.) and anhydrous benzoylcarbinol * (5 g.) in dry ether (70 c.c.), which was then gently refluxed for 14 hours. The filtered solution was freed from ether under diminished pressure, a solution of the syrupy residue in acetone (50 c.c.) poured in a fine stream into cold water, and the precipitated viscous mass triturated with fresh water until it crystallised. The dried material was crystallised several times from 86% methyl alcohol (charcoal) and finally obtained in white, prismatic needles, m. p. 104—105° (yield of pure product, 4 g.) (Found: C, 56·4; H, 5·7. $C_{22}H_{26}O_{11}$ requires C, 56·6; H, 5·6%). The substance is moderately readily soluble in cold methyl or ethyl alcohol and is easily soluble in the hot solvents. At room temperature, 100 c.c. of dry ether dissolve about 1·2 g. of the glucoside. The condensation may also be effected in the cold and without a solvent and, though the process is slower than that described above, the yield is about the same.

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* Hudson (*J. Amer. Chem. Soc.*, 1924, **46**, 466, 979, 2501) indicated that this substance, the so-called acetobromoglucose, is probably an α-glucose derivative and yields β-glucosides through a Walden inversion.

3-β-*Glucosidoxy-7-hydroxyflavylium Chloride* (II).—Condensation of tetra-acetylglucosidoxyacetophenone and β-resorcylaldehyde in presence of hydrogen chloride occurs in absolute formic acid solution, but the product is contaminated with the sugar-free pyrylium salt. Trials showed, however, that in ethereal solution the hydrolysis of the glucoside does not occur in 96 hours, although in this case the reaction is very sluggish. A cooled solution of tetra-acetylglucosidoxyacetophenone (1 g.) and β-resorcylaldehyde (1·5 g.) in dry ether (100 c.c.) was saturated with hydrogen chloride and allowed to remain for 96 hours. The dark brown, viscous mass obtained on the addition of light petroleum was separated, washed with ether, and dried in a vacuum; it became a brittle solid which could not be crystallised. Deacetylation was effected by means of saturated methyl-alcoholic ammonia at 0° during 14—15 hours, the ammonia and methyl alcohol being then removed below 25° under diminished pressure. The residue was dissolved in 2% methyl-alcoholic hydrogen chloride (40 c.c.), and the glucoside precipitated from the filtered solution by the addition of ether (300 c.c.). The amorphous products from several experiments were combined and dried in a vacuum. A mixture of the crude material (4 g.), methyl alcohol (50 c.c.), and 12% hydrochloric acid (5 c.c.) was heated to the boiling point for 1 minute, a large proportion of the impurities being thus dissolved, and filtered hot.

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* Benzoylcarbinol was prepared by the method of O. Fischer and Busch (*Ber.*, 1891, **24**, 2680) from ω-bromoacetophenone, the yield being 80%. The hydroxyketone was not, however, isolated by means of ether, but was separated from an aqueous solution by the addition of potassium carbonate. It was dehydrated by distillation of a solution in a large volume of benzene and finally crystallised from light petroleum in glistening plates, m. p. 85—86°.

The orange-red residue was easily soluble in 2% hydrochloric acid and in 2% methyl-alcoholic hydrogen chloride. The glucoside (2 g.) was dissolved in a hot mixture of methyl alcohol (15 c.c.) and 2% hydrochloric acid (10 c.c.), and the filtered solution allowed to remain for 24 hours. Most of the alcohol evaporated and crystals were deposited; the process was thrice repeated, and the salt obtained in bundles of microscopic, pointed rods which matted together on the filter and when dry exhibited a golden reflex. The salt was dried for 3 hours, powdered, and again dried in a vacuum for 15 hours (Found: C, 56·6; H, 5·0; Cl, 8·2, 7·8. $C_{21}H_{21}O_8Cl,0{\cdot}5H_2O$ requires C, 56·6; H, 4·9; Cl, 8·0%). The substance is readily soluble in 2% and 4% hydrochloric acid and in the simple alcohols to orange solutions which become red on the addition of sodium acetate. Pseudo-base formation was observed and the salt is only partly extracted from an aqueous acid solution by means of *iso*amyl alcohol. On boiling with 15% hydrochloric acid for 5 minutes, hydrolysis occurred and, after cooling, 3 : 7-dihydroxyflavylium chloride separated from the solution in orange-brown prisms. The salt was identified by comparison with an authentic specimen.

3 : 7-*Dihydroxyflavylium Chloride* (III).—(A). A solution of β-resorcylaldehyde (1·0 g.) and ω-acetoxyacetophenone (1·2 g.) in formic acid (20 c.c.) was saturated with hydrogen chloride. A week later, the crude product was isolated after precipitation by ether and boiled with 0·2% hydrochloric acid, and the solution filtered. Concentrated hydrochloric acid was then added, bringing the acid concentration to about 8%, and, on cooling, the salt crystallised in deep orange-brown, elongated, rhombic, pointed prisms (yield, 0·3 g.) (Found in material dried in a vacuum: C, 61·6; H, 4·4. Calc. for $C_{15}H_{11}O_3Cl,H_2O$: C, 61·5; H, 4·5%).

(B). The condensation of β-resorcylaldehyde (0·5 g.) and benzoylcarbinol (0·5 g.) in formic acid (20 c.c.) by means of hydrogen chloride occupied 72 hours and the yield of the pure salt was 0·35 g., about twice as great as that obtained from ω-acetoxyacetophenone. The properties of the salt were in agreement with those described by Pratt and Robinson (*loc. cit.*).

4-O-*Tetra-acetylglucosidoxy*-2-*hydroxybenzaldehyde* (IV).—A solution of potassium hydroxide (2·6 g.) in water (25 c.c.) cooled to 10° was gradually added to one of β-resorcylaldehyde (6 g.) and *O*-tetra-acetylglucosidyl bromide (18 g.) in pure acetone (55 c.c.), the temperature being maintained below 16° by cooling in ice-water. Two layers appeared and, after 30 minutes, acetone (20 c.c.) was added and the homogeneous solution was allowed to remain for 12 hours. The liquid was rendered faintly acid by the addition of a little dilute acetic acid, and the acetone removed in a vacuum below 25°. The thick residual syrup, which became semi-solid on trituration with cold water, was several times crystallised (charcoal) from 85% methyl alcohol; it was finally obtained in almost colourless, silky, prismatic needles, m. p. 134—135° (Found: C, 53·5; H, 5·1. $C_{21}H_{24}O_{12}$ requires C, 53·8; H, 5·1%). (A mixture with β-resorcylaldehyde, also m. p. 135°, had m. p. 90—100°.) This acetylglucoside is moderately readily soluble in methyl or ethyl alcohol, sparingly soluble in cold 85% methyl alcohol, and very readily soluble in hot alcohol. 100 C.c. of dry ether dissolve about 1 g. at room temperature. Ferric chloride added to an alcoholic solution gives a dark red coloration identical with that developed by 2-hydroxy-4-methoxybenzaldehyde under similar conditions. The residues from this preparation were examined, but an isomeric compound could not be isolated.

7-*Glucosidoxy*-3 : 3′ : 4′-*trimethoxyflavylium Chloride* (V).—A solution of tetra-acetylglucosidoxyhydroxybenzaldehyde (2 g.) and ω-methoxyacetoveratrone (3 g., an excess) in dry ether (200 c.c.) was saturated with hydrogen chloride at 16—18° and allowed to remain for 72 hours. Almost the whole of the product crystallised in compact clusters of slender, prismatic needles which were dark brown in mass (yield, 2 g.). Recrystallisation from 0·5% hydrochloric acid could not be satisfactorily accomplished owing to the tendency of the substance to give a crystalline, colourless pseudobase, whilst with more concentrated acid deacetylation appeared to occur; moreover, in 2% to 4% hydrochloric acid the salt was only sparingly soluble to an orange-red solution. A solution of the acetylglucoside (2 g.) in methyl alcohol (150 c.c.) was saturated at 0° with ammonia and allowed to remain at 0° for 14 hours; the ammonia and methyl alcohol were then removed under diminished pressure and below 20° until the volume was about 15 c.c. Hydrochloric acid (30 c.c. of 4%) at 50° was added and, on cooling, the chloride separated in crimson, rhombic plates (yield, 1·5 g.) which exhibited a brilliant golden reflex. Recrystallisation in a similar form was effected by dissolving 1 g. in hot methyl alcohol (15 c.c.), adding warm 4% hydrochloric acid (30 c.c.), heating the mixture to 60—70° (it must not be boiled) and filtering it. The salt was dried in a high vacuum for 48 hours (Found: C, 54·2; H, 5·7; Cl, 6·7. $C_{24}H_{27}O_{10}Cl,H_2O$ requires C, 54·5; H, 5·5; Cl, 6·8%). Concentrated acid solutions are crimson and dilute solutions are orange-red. This glucoside is readily hydrolysed, even by 4% hydrochloric acid, and on being treated in the usual way with boiling 15% hydrochloric acid it yielded fisetinidin chloride trimethyl ether, which was identified by comparison with an authentic specimen (Pratt and Robinson, *loc. cit.*). The *picrate* of the glucoside separated from a warm alcoholic solution of the chloride and picric acid in fine needles and crystallised from 85% ethyl alcohol, containing a little picric acid, in balls of bright red, very slender, prismatic needles which filled the liquid. On heating, decomposition commenced at 240—243° and was complete at 250—252°. In contrast, the acetylated glucoside did not yield a stable picrate.

We desire to thank the International Education Board of New York for a Fellowship which has enabled one of us to take part in the investigation, and the Government Grant Committee of the Royal Society for a grant which has defrayed a part of the expense of the work.

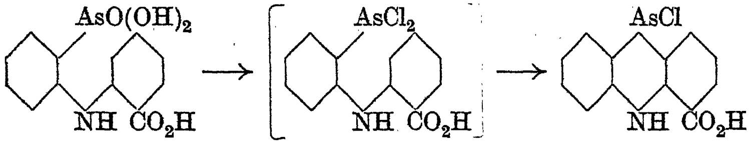
THE UNIVERSITY, MANCHESTER. [*Received, December 10th*, 1926.]

XXXIX.—10-*Chloro*-5 : 10-*dihydrophenarsazine and its Derivatives. Part IV. Carboxy-derivatives.*

By HAROLD BURTON and CHARLES STANLEY GIBSON.

APART from the synthesis of 10-chloro-5 : 10-dihydrophenarsazine (J., 1926, 452), the parent substance and all its analogues so far described have been prepared by the action of arsenious chloride on diphenylamine and its analogues, respectively (*ibid.*, pp. 450, 464, 2241, where all references are given). Owing to the difficulty of obtaining diphenylaminomonocarboxylic acids, carboxy-derivatives of 10-chloro-5 : 10-dihydrophenarsazine could not be obtained directly and it was necessary to study the condensation of *o*-bromophenylarsinic acid with different aminobenzoic acids.

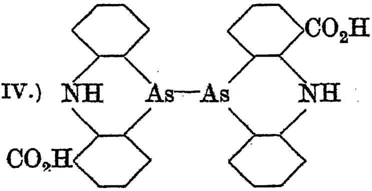
Anthranilic acid condenses readily with *o*-bromophenylarsinic acid in boiling nitrobenzene in presence of anhydrous potassium carbonate and a small quantity of copper powder, forming 2-*carboxydiphenylamine*-6′-*arsinic acid* (I). This acid, on reduction with sulphur dioxide in alcoholic-hydrochloric acid solution, is readily converted into 2-*carboxydiphenylamine*-6′-*arsenic dichloride* (II), which, however, cannot be isolated in the pure condition owing to the ease with which it loses hydrogen chloride. Complete conversion of this compound into 10-*chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid* (III) can be accomplished either by boiling the acetic acid solution of the reduction product or by dissolving the latter in hot sodium hydroxide solution, boiling for a few minutes, and then precipitating the final product by the addition of an excess of concentrated hydrochloric acid.

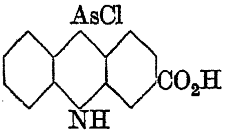


(I.) (II.) (III.)

Whilst its solubility in neutral solvents is much less, as far as its chemical properties are concerned, 10-chloro-5 : 10-dihydrophenarsazine-4-carboxylic acid is very similar to the parent compound. When reduced with hypophosphorous acid, it yields a cacodyl derivative, *viz.*, 10 : 10′-*bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine* (IV), and this compound is soluble in sodium hydroxide.

(IV.)





(V.)

By a similar procedure, starting from *m*-aminobenzoic acid and *o*-bromophenylarsinic acid, 10-*chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic acid* (V) was obtained which was even less soluble than the isomeric compound.

We have not succeeded in isolating the corresponding condensation products, using *p*-aminobenzoic acid and *N*-methylanthranilic acid.

EXPERIMENTAL.

2-*Carboxydiphenylamine*-6′-*arsinic Acid* (I).—A mixture of anthranilic acid (13·6 g.), *o*-bromophenylarsinic acid (14·0 g.), anhydrous potassium carbonate (14·0 g.), nitrobenzene (100 c.c.), and a trace of copper powder was boiled under reflux for 7 hours. After all volatile matter had been removed by distillation in steam, the resulting solution was boiled with charcoal, filtered, and acidified. The crude acid (11·0 g.) crystallised from acetic acid in colourless, silky needles, m. p. 243° (decomp.) (Found : As, 22·3. $C_{13}H_{12}O_5NAs$ requires As, 22·25%).

Reduction of 2-*Carboxydiphenylamine*-6′-*arsinic Acid.*—A solution of the acid (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine was heated to boiling, and sulphur dioxide passed into it for a few minutes. A yellow precipitate formed immediately. The mixture was cooled rapidly, and the solid material separated. This substance was not homogeneous, since on recrystallisation from acetic acid it gave two types of crystals, yellow needles and transparent needles. This result indicated that reduction had taken place and that a partial elimination of hydrogen chloride had been effected.

10-*Chloro*-5 : 10-*dihydrophenarsazine*-4-*carboxylic acid* (III) was prepared by working up the crude reduction product in two ways : (*a*) A solution of the crude reduction product in the minimum quantity of hot acetic acid was boiled under reflux for 3 hours. On cooling, a homogeneous mass of yellow crystals separated. These were recrystallised from acetic acid and obtained in yellow needles, m. p. 243° (decomp.). (*b*) The crude material from the reduction of 5 g. of the original acid was dissolved in 3*N*-sodium hydroxide (75 c.c.), and the colourless solution boiled for a few minutes. On acidifying the cold solution with an excess of concentrated hydrochloric acid, the product separated as a yellow powder. This, after recrystallisation from acetic acid, was identical with the product previously obtained (Found: As, 23·4. $C_{13}H_9O_2NClAs$ requires As, 23·3%).

10 : 10′-*Bis*-4-*carboxy*-5 : 10-*dihydrophenarsazine* (IV).—A solution of 10-chloro-5 : 10-dihydrophenarsazine-4-carboxylic acid (2 g.) in acetic acid (20 c.c.) containing a trace of iodine was mixed with a solution of hypophosphorous acid (5 c.c.; *d* 1·136). Almost immediately an orange-coloured precipitate separated. This was filtered off, washed with acetone, and dried. The compound, m. p. 253° (decomp.), was practically insoluble in the usual organic solvents, but dissolved in sodium hydroxide, giving an orange-coloured solution (Found: As, 25·9. $C_{26}H_{18}O_4N_2As_2$ requires As, 26·2%).

3-*Carboxydiphenylamine*-6′-*arsinic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot AsO(OH)_2,$$

was prepared from *o*-bromophenylarsinic acid and *m*-aminobenzoic acid in a similar manner to the corresponding 2-carboxydiphenylamine-6′-arsinic acid, amyl alcohol being used instead of nitrobenzene for the condensation. It crystallised from dilute acetic acid in colourless needles, m. p. 238—239° (decomp.) (Found: As, 21·9. $C_{13}H_{12}O_5NAs$ requires As, 22·25%).

10-*Chloro*-5 : 10-*dihydrophenarsazine*-3-*carboxylic Acid* (V).—The reduction of 3-carboxydiphenylamine-6′-arsinic acid was carried out in a similar manner to that of the isomeride. The crude chloro-compound was dissolved in hot sodium hydroxide solution, and precipitated from the cold solution with an excess of concentrated hydrochloric acid. The yellow precipitate was very sparingly soluble in all organic solvents and therefore difficult to obtain pure. It did not melt below 300° (Found: As, 22·8. $C_{13}H_9O_2NClAs$ requires As, 23·2%).

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[*Received, December 7th*, 1926.]

XL.—*The Nature of the Alternating Effect in Carbon Chains. Part X. The Nitration of Some Derivatives of β-Phenylethylamine.**

By FRANK ROBERT GOSS, WALTHER HANHART, and CHRISTOPHER KELK INGOLD.

To facilitate the development of the theory of reactivity-transmission by the Lewis electron-displacement mechanism, Goss, Ingold, and Wilson's quantitative study of the substitution of benzylamine derivatives (J., 1926, 2440) has now been supplemented by a similar study of the nitration of some derivatives of β-phenylethylamine. Here the electron-attracting centre is separated from the nucleus by an additional methylene group, and its *m*-directive effect should accordingly be weaker.

Experience having shown that the replacement of one alkyl group by another in a secondary, a tertiary, or a quaternary benzylamine has a relatively small influence on the degree of *m*-substitution observed in each class (*loc. cit.*), we have restricted the present investigation of β-phenylethylamine derivatives to an examination of the primary base, and one secondary, one tertiary, and one quaternary derivative. The results are in the following table, in which the data for the corresponding derivatives of benzylamine also are set forth for comparison.

Nitration of Derivatives of Benzylamine and β-*Phenylethylamine in Nitric Acid* (d 1·5) *at* −10° to 0°.

Benzylamine bases.		β-Phenylethylamine bases.	
Side chain.	Proportion of *m*-substitution.	Side chain.	Proportion of *m*-substitution.
$-CH_2\cdot NH_2$	49%	$-CH_2\cdot CH_2\cdot NH_2$	12%
$-CH_2\cdot NHMe$	69 ,,	$-CH_2\cdot CH_2\cdot NHMe$	15 ,,
$-CH_2\cdot NMe_2$	58 ,,	$-CH_2\cdot CH_2\cdot NMe_2$	13 ,,
$-CH_2\cdot NMe_3{}^+$	88 ,, †	$-CH_2\cdot CH_2\cdot NMe_3{}^+$	19 ,, †

† Picrate used.

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* These experiments and a corresponding series on γ-phenylpropylamine derivatives were completed in all essentials at the date of the appearance of Ing and Robinson's statement (J., 1926, 1656) that they were investigating a compound of each class.

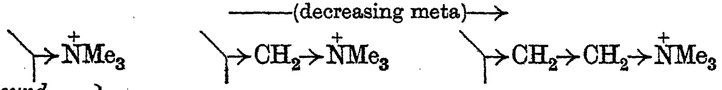
From these figures, it will be evident that the effect originating in the positively charged nitrogen atom suffers such loss by transmission through the additional carbon atom that the resulting *m*-substitution is diminished in ratios of approximately 1/4—1/5.

β-Phenylethylamine has been previously nitrated by Ehrlich and Pistschimuka (*Ber.*, 1912, **45**, 2428), who isolated the *p*-nitro-compound and one other product which they regarded as the *m*-derivative (yield 18%; m. p. of hydrochloride "gegen 160°"). We think, however, that this could not have been the pure *m*-compound, since our specimen of its hydrochloride melts 45° higher. On the other hand, the m. p. and properties of Ehrlich and Pistschimuka's product agree almost exactly with those of our *o*-compound. Further, the quantity of "meta-" derivative obtained by Ehrlich and Pistschimuka is 1½ times as great as the total amount (12%) estimated to be contained in our nitration products, and experience of the separation of the three isomerides has left us with the impression that it would be difficult to isolate in the pure condition more than a moderate fraction of the quantity of *m*-derivative actually present. On the other hand, the proportion of the *o*-compound formed on nitration under our conditions is considerably greater (25%), and therefore it might be possible to isolate as much as 18% of this substance. Methyl-β-phenylethylamine does not appear to have been nitrated previously. Dimethyl-β-phenylethylamine was nitrated by Barger (J., 1909, **95**, 2195), who obtained the *p*-compound; we have also separated some of the *m*-isomeride, and have isolated all three isomerides from the nitration product of trimethyl-β-phenylethylammonium picrate.

The figures in the last column of the table are based on the weights of unrecrystallised *m*-nitrobenzoic acid separated as previously described (Baker and Ingold, J., 1926, 2462) from the mixtures of nitrobenzoic acids formed by oxidation, either of the original mono-nitration products or of the residues remaining after partial separations of pure isomerides. The oxidation yields were mostly quantitative and the separation of the acids was again checked on artificial mixtures and was shown to give results correct to about 1·5%. Also by oxidation of the pure *o*-, *m*-, and *p*-isomerides it was shown that each gave the same (generally quantitative) yield of the corresponding nitrobenzoic acid; further, by oxidation of artificial mixtures of isomeric nitro-bases of similar composition to the nitration products, and subsequent separation of the acids, the proportions of the isomerides were satisfactorily estimated; it is therefore hoped that the figures submitted are not seriously in error.

Summarising these results, then, it appears that the work now described provides the first clear proof of the formation of *m*-derivatives by direct nuclear substitution of β-phenylethylammonium compounds, and we can recall no other example of *m*-substitution in which the *m*-directing group is separated from the nucleus by two saturated carbon atoms. Further, the new results combined with those obtained by Vorländer and Siebert (*Ber.*, 1919, **52**, 294) for quaternary derivatives of aniline provide the first experimental evidence that the directive effect of an ionic centre situated in a side-chain consisting otherwise of saturated carbon atoms does not alternate, but diminishes continuously with increasing distance from the nucleus * :

Theoretical Order :



$$\xrightarrow{\text{(decreasing meta)}}$$

$$\rightarrow \overset{+}{N}Me_3 \qquad \rightarrow CH_2 \rightarrow \overset{+}{N}Me_3 \qquad \rightarrow CH_2 \rightarrow CH_2 \rightarrow \overset{+}{N}Me_3$$

Found (% meta) : } 100 88 19

The lower values for the primary, secondary, and tertiary β-phenylethylamine salts, as compared with that obtained for the quaternary salt, are attributed to partial compensation by the negative end of the dipolar group (Goss, Ingold, and Wilson, *loc. cit.*; and following paper).

EXPERIMENTAL.

(A) *Nitration of β-Phenylethylamine.*

(i) *Qualitative Separation of Isomerides.*—The base (10 g.) was run in the course of 1·5 hours into nitric acid (50 c.c.; d^{15° 1·50) at −10°. Nitration appeared to follow almost instantaneously, but the mixture was warmed to 0° before being mixed with ice and basified with sodium hydroxide. The products then extracted with ether were isolated as their hydrochlorides by re-extracting the ethereal solution with sufficient dilute hydrochloric acid and evaporating this solution to dryness (Found: Cl, 17·4. $C_8H_{10}O_2N_2,HCl$ requires Cl, 17·5%).

A single crystallisation from the minimal quantity of boiling 95% alcohol yielded 8·7 g. of almost colourless plates, m. p. 209—210°. This is the recorded m. p. of *p*-nitro-β-phenylethylammonium chloride. On oxidation by permanganate, *p*-nitrobenzoic acid was formed (yield 99%; m. p. 230—231°; mixed m. p. 232—233°). A further 1·0 g. of the same hydrochloride was obtained from the residue remaining on evaporation of the alcoholic mother-liquor by

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* Mr. I. S. Wilson has obtained the approximate value 5 ± 2% for $\rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_2 \rightarrow \overset{+}{N}Me_3$ by nitration of the picrate under similar conditions.

diluting its solution in the minimal quantity of boiling absolute alcohol with 800 c.c. of chloroform and allowing 24 hours for crystallisation; in another otherwise identical experiment the same result was achieved by extracting the residue with a warm alcohol–chloroform mixture (1 : 4), in which the *p*-compound remains undissolved. Total yield, 58%.

The *o*-derivative was next isolated by evaporating the chloroform and alcohol, and crystallising the residue from a small quantity of absolute alcohol at 0°. The crystals obtained were washed with alcohol–chloroform and the undissolved portion was crystallised 2—3 times from ethyl acetate containing the minimal quantity of alcohol necessary for solution (yields, up to 9%). o-*Nitro-β-phenylethylammonium chloride* crystallises as flattened needles or leaflets, m. p. 162—163° (Found: C, 47·1; H, 5·9. $C_8H_{11}O_2N_2Cl$ requires C, 47·4; H, 5·4%). On oxidation with potassium permanganate, it gives *o*-nitrobenzoic acid. (Yield of unpurified acid, 100%; m. p. 140—141°; mixed m. p. with genuine *o*-acid 141—144°, and with genuine *m*-acid 100—110°; after crystallisation from water, m. p. 141°; after crystallisation from chloroform, m. p. 144—145° and mixed m. p.'s with the *o*- and *m*-acids 144—145° and 105—110°, respectively. These particulars are recorded because Ehrlich and Pistschimuka, by oxidising their "meta" salt, obtained an acid which, after crystallisation from water, had m. p. 140°. This is the m. p. of pure *m*-nitrobenzoic acid, but it is also that of the *o*-nitrobenzoic acid obtained by us by oxidation and crystallised from water.)

The genuine *m*-derivative was isolated as its *oxalate* by basifying the residue from the combined mother-liquors with sodium hydroxide, extracting it with ether, precipitating the salt with anhydrous oxalic acid in dry ethereal solution, and crystallising it from 90% alcohol until the m. p. rose to and remained constant at 200° (decomp.) (Found: C, 46·7; H, 4·8. $C_{10}H_{12}O_6N_2$ requires C, 46·9; H, 4·7%). m-*Nitro-β-phenylethylammonium chloride*, which separates from alcohol in platelets or flattened needles, has m. p. 204—205° (Found: C, 47·5; H, 5·5; N, 13·6. $C_8H_{11}O_2N_2Cl$ requires C, 47·4; H, 5·4; N, 13·8%). On oxidation by permanganate, *m*-nitrobenzoic acid was obtained. (Yield, before purification, 102%; m. p. 131—135°; mixed m. p. with genuine *m*-acid 138—140°, and with *o*-acid 100—110°; after one crystallisation from ethyl acetate–ligroin, m. p. 139—140°, mixed m. p. with *m*-acid, 139—140°, and with *o*-acid 105—115°.)

(ii) *Estimation of Isomerides*.—Since the three isomerides can be oxidised practically quantitatively to the readily separable nitrobenzoic acids, it was decided to employ that method (Baker and Ingold, *loc. cit.*) for the estimation of the proportions, although, preliminary experiments having shown that the *o*- and *p*-derivatives do not lose their side chains on reduction and subsequent bromination, it is probable that this method also would have worked (Goss, Ingold, and Wilson, *loc. cit.*).

(*a*) The base (10·00 g.) was nitrated as described above, and the main quantity of *p*-nitro-derivative removed as hydrochloride (7·68 g. = 46%). The residues (7·48 g. = 45%) were intimately ground and 2·00 g. were oxidised by gradually adding the theoretical quantity of 3% permanganate solution to a boiling solution of the salt in 200 g. of water, the addition being timed to keep pace with decolorisation. The yield of mixed acids was 1·60 g. (=97%) (Found : *M*, 167. Calc. : *M*, 167. Benzoic acid, by sublimation, 0·25%). The separation was performed with 1·512 g. after the removal of the benzoic acid. The *p*-acid (21%) * had m. p. 232°, mixed m. p. 233—235°; the *m*-acid (26%) * had m. p. 130°, mixed m. p. 136—138°, and, after one crystallisation from ligroin–ethyl acetate, m. p. 139—140°. Hence the original nitration product is estimated to have contained, *para* = (46 + 0·21 × 45)/91 = 61%; *meta* = 0·26 × 45/91 = 13%; *ortho* (by difference only) =26%.

An artificial mixture of the *p*-, *m*-, and *o*-hydrochlorides in the respective proportions 62·3%, 14·1%, 23·6%, on oxidation gave nitrobenzoic acids (yield 99%), which on separation yielded 61·7% of *p*-acid, m. p. 230—234°, mixed m. p. 234—235°, and 13·0% of *m*-acid, m. p. 132—133°, mixed m. p. 137—139°.

(*b*) The base (10·00 g.) was nitrated, and the diluted acid solution was extracted with ether, basified with alkali, and then again extracted. The second extract was dried with sodium sulphate, precipitated with dry hydrogen chloride, and then completely evaporated. The residue (16·3 g. = 97%) after grinding was oxidised (2·00 g.) as before (yield 1·61 g. = 98%; *M*, 168; benzoic acid, nil), and the isomeric acids were separated. The *p*-acid (65%) had m. p. 229—234°, mixed m. p. 232—235°; and the *m*-acid (11%) had m. p. 129—133°, mixed m. p. 138—140°.

(*c*) A portion (10·00 g.) of the mixed hydrochlorides obtained in experiment (*b*) was separated into 5·01 g. of *p*-nitro-β-phenylethylammonium chloride and 4·97 g. of residues (0·02 g. lost). The residues were oxidised as usual (yield 4·03 g. = 98·5%; *M*, 166, 166; benzoic acid 0·35%), and the acids separated. The *p*-acid (28%) had m. p. 234—235°, mixed m. p. 234—235°; the *m*-acid (26%) had m. p. 133—136°, mixed m. p. 139—140°. Hence the original mixture is estimated to have contained, *para* = (50·1 + 49·7 × 0·28)/99·8 = 64%; *meta* = 49·7 × 0·26/99·8 = 13%; *ortho* (by difference) 23%.

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* These and the other percentages of *p*- and *m*-nitrobenzoic acids given in this section are already corrected for the solubility of the *p*-acid and the *m*-barium salt (Baker and Ingold, *loc. cit.*).

(B) *Nitration of Methyl-β-phenylethylamine.*

(*d*) The base (4·5 g.) was nitrated at −10° to −5° with 30 g. of nitric acid (*d* 1·5), the conditions being otherwise as described for experiment (*a*); the product (yield 97·5%) was isolated as hydrochlorides, as in experiment (*b*), and oxidised in the usual way. The mixed nitrobenzoic acids (yield 101%; *M*, 167, 168; benzoic acid, nil) on separation contained *p*-nitrobenzoic acid (61%) having m. p. 233—234°, mixed m. p. 234—235°, and *m*-nitrobenzoic acid (15%), m. p. 125—135°, mixed m. p. 139—140°, m. p. after one crystallisation 140°.

(*e*) The picrate (m. p. 140—141°; Johnson and Guest, *Amer. Chem. J.*, 1909, **42**, 340) of the base was nitrated in 7·5 parts of nitric acid (*d* 1·50) at −10° to −5° and the product was mixed with ice, extracted with benzene, basified and extracted with ether. The residue from the ether on precipitation in benzene solution with picric acid gave 93·2% of mixed picrates. These were oxidised as usual (excepting that permanganate sufficient to destroy the picrate ions was added rapidly, and only the remaining quantity cautiously) and gave 97·6% of mixed acids (*M*, 166, 167. Benzoic acid, nil). The separated *p*-acid (65%) had m. p. 230—235°, mixed m. p. 233—235°, and the *m*-acid (15%) m. p. 125—135°, mixed m. p. 139—140°.

(C) *Nitration of Dimethyl-β-phenylethylamine.*

(i) *Qualitative Separation of Isomerides.*—The base was nitrated in the form of its picrate (7·5 g.) with nitric acid (45 g.; *d* 1·50) at −10°, and at the end of the process the temperature was allowed to rise to 0°; ice was then added, and, after extraction of the picric acid and any neutral by-products with benzene, the nitro-bases were liberated with sodium hydroxide and extracted with ether. In one experiment, the product (yield 90%) was isolated as picrates, and in another as oxalates, by precipitation in each case with the appropriate acid in dry benzene and ether respectively.

Dimethyl-*p*-nitrophenylethylammonium oxalate (Barger, J., 1909, **95**, 2195) may be obtained from the mixed oxalates, but owing to the sparing solubility of the *m*-oxalate, this method is less satisfactory than the separation of the *p*-nitro-picrate from the mixed picrates, by crystallisation from acetone–benzene (1 : 6) or acetone–alcohol. *Dimethyl-*p*-nitro-β-phenylethylammonium picrate* crystallises both in well-defined needles and in cubes, the latter modification being apparently the more stable, m. p. 162° (Found : C, 45·1 ; H, 4·1. $C_{16}H_{17}O_9N_5$ requires C, 45·4 ; H, 4·0%). Oxidation with permanganate gave *p*-nitrobenzoic acid (yield 100% ; m. p. 234—235°).

The same compounds were prepared from the primary salts as follows. *p*-Nitro-β-phenylethylammonium chloride (8 g.) and 38% aqueous formaldehyde (16 c.c.) were heated together at 135° for 3 hours, and the bases liberated by the addition of sodium hydroxide to the cooled solution extracted with ether. The oxalate, m. p. 154°, precipitated by the addition of dry ethereal oxalic acid was identical with the separated oxalate (above), and the similarly prepared picrate with the separated picrate.

*Dimethyl-*m*-nitro-β-phenylethylammonium oxalate* was isolated from the oxalate mixture by repeatedly crystallising it from 95% alcohol and diluting the filtrates of the later crystallisations with 100% alcohol; needles, m. p. 186°, then separated (Found : C, 50·5 ; H, 5·7. $C_{12}H_{16}O_6N_2$ requires C, 50·7 ; H, 5·7%). The *picrate*, prepared by precipitation of an alcoholic solution of the oxalate with picric acid, formed stout needles or prisms, m. p. 166—167° (Found : C, 45·4 ; H, 4·4. $C_{16}H_{17}O_9N_5$ requires C, 45·4 ; H, 4·0%). On oxidation of the oxalate with nitric acid, *m*-nitrobenzoic acid was obtained, and the same acid (m. p. 134—138°, mixed m. p. 139—140°) was obtained in 99% yield by the action of permanganate on the picrate.

We did not encounter the *o*-nitro-salts in the course of the above separations, but in order to study its behaviour on oxidation, we prepared *dimethyl-*o*-nitro-β-phenylethylammonium picrate* from the hydrochloride of the primary *o*-nitro-base by the formaldehyde method described above. The salt crystallised from alcohol–acetone in yellow prisms, m. p. 160—161° (Found : C, 45·8 ; H, 4·1. $C_{16}H_{17}O_9N_5$ requires C, 45·4 ; H, 4·0%). On oxidation with permanganate by the usual method, it gave *o*-nitrobenzoic acid. (Yield, unpurified, 102% ; m. p. 138—142°, mixed m. p. 140—143° ; crystallised from chloroform, m. p. 146°, mixed m. p. 146°.) Although the three isomeric picrates melt at not very different temperatures, they depress each other's m. p. by 15—30°.

(ii) *Estimation of Isomerides.*—(*f*) The nitration product isolated in the form of picrates (yield 93% ; Found : C, 45·5 ; H, 4·3. Calc. : C, 45·4 ; H, 4·0%), on oxidation as usual, gave nitrobenzoic acids in 101% yield (*M*, 168 ; benzoic acid, nil). A sample of the mixture on separation was found to contain 70% of *p*-nitrobenzoic acid (m. p. 234—235°, mixed m. p. 234—235°) and 12% of *m*-nitrobenzoic acid (m. p. 120—130°, mixed m. p. 133—136° ; crystallised once, m. p. 139—140°, mixed m. p. 140°).

(*g*) By crystallisation from acetone–benzene the mixed picrates were divided into two portions constituting 66% and 34% of the whole. The first, on oxidation, gave acids (yield 100%; benzoic acid, nil) which, on separation, contained *p*-nitrobenzoic acid (yield 85%) having m. p. 232—233°, and mixed m. p. 233—238°, and *m*-nitrobenzoic acid (yield 11%) having m. p. 128—133°, mixed m. p. 136—138°. The second gave acids (yield 101%; benzoic acid 1·2%; *M*, 165, 166) which contained the *p*-acid (30%), m. p. 220—232°, mixed m. p. 225—235°, and the *m*-acid (19%), m. p. 130—137°, mixed m. p. 139—140°. The original mixture is therefore estimated to have contained *para* 66%, *meta* 14%, *ortho* (by difference) 20%.

(D) *Nitration of Trimethyl-β-phenylethylammonium Picrate.*

(i) *Qualitative Separation of Isomerides.*—Trimethyl-β-phenylethylammonium picrate (Decker and Becker, *Ber.*, 1912, **45**, 2404) was nitrated in nitric acid at —1—0°, and the nitric acid solution was warmed to 15°, mixed with ice (picric acid separated), just basified with concentrated sodium hydroxide solution, and cooled to —10°; the nitro-picrates then separated (α; yield 92%). The filtrate, on saturation with sodium picrate, yielded a further small quantity of crystalline material (β), and more was obtained from the mother-liquor by concentration and extraction with ethyl acetate (γ). The aqueous solution was finally evaporated to dryness, and the residue extracted with alcohol (δ).

The mixture (α), on crystallising twice from boiling alcohol, yielded pure *trimethyl*-p-*nitro*-β-*phenylethylammonium picrate* as yellow leaflets, m. p. 144—145° (yield 50%) (Found: C, 46·4; H, 4·5. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·4%). The corresponding *iodide* forms pale yellow needles, m. p. 206° (Found: I, 37·5. $C_{11}H_{17}O_2N_2I$ requires I, 37·8%). This was prepared by boiling a benzene solution of dimethyl-*p*-nitrophenylethylamine (from 1·5 g. of oxalate) with sodium carbonate (2 g.) and methyl iodide (2·3 c.c.) for 3 hours, washing the salts with hot benzene, and extracting the quaternary iodide with hot alcohol, from which it separated on cooling. The above picrate was also prepared from *p*-nitrophenylethylammonium chloride (0·75 g.) by boiling its solution in absolute alcohol (20 c.c.) for 2 hours with methyl sulphate (2·5 c.c.) and sodium carbonate (2 g.). After water had been added, and the alcohol boiled off, the solution was extracted with ether, and the quaternary picrate precipitated by addition of a solution of sodium picrate to the aqueous solution (yield 55%). On oxidation by permanganate *p*-nitrobenzoic acid was formed (yield 100%; m. p. 230—235°; mixed m. p. 232—235°).

The mixtures (β), (γ), and (δ) contained sodium salts, from the bulk of which they were freed by washing with cold water. The products thus partly purified were crystallised *slowly* from boiling alcohol or water, and the three isomerides separated by mechanical means. The *p*-picrate was the only one which separated in plates; the other two formed needles, but those of the *o*-compound were of a paler yellow colour than those of the *m*-isomeride.

Trimethyl-m-*nitro*-β-*phenylethylammonium picrate* separates from alcohol in short needles (especially when slightly impure), and when pure, in felted masses of flexible, hair-like crystals, m. p. 147—148° (Found: C, 46·7; H, 4·5. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·4%). Mixtures with the *o*- and *p*-isomerides melted at about 125°. The same substance was prepared from *m*-nitro-β-phenylethylammonium chloride by methylation with methyl sulphate as described above. On oxidation by permanganate *m*-nitrobenzoic acid was obtained in 100% yield (m. p. 135—136°; mixed m. p. 139—140°).

The *trimethyl*-o-*nitro*-β-*phenylethylammonium picrate* obtained as described above was identical with the picrate obtained from the product of the action of the alcoholic methyl sulphate and sodium carbonate on *o*-nitro-β-phenylethylammonium chloride, and with the picrate which was precipitated when *o*-nitro-β-phenylethyldimethylamine was mixed with *s*-trinitroanisole in benzene solution. Crystallised from alcohol, it formed bright yellow, brittle needles, m. p. 146—147° (Found: C, 46·7; H, 4·5. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·4%). The yield of *o*-nitrobenzoic acid (m. p. 145—147°; mixed m. p. 145—147°; mixed m. p. with *m*-nitrobenzoic acid 110—120°) obtained on oxidation by permanganate was 100%.

(ii) *Estimation of Isomerides.*—(*h*) The quaternary picrate (8·00 g.) was added to 60 g. of nitric acid ($d^{16°}$ 1·50) at—5° during 10 minutes, and the product was warmed to 10° during 5 minutes, kept at 10° for 15 minutes, and then mixed with ice and worked up for the *p*-compound as described above. The pure *p*-compound isolated weighed 4·75 g., and the combined residues, when freed from sodium salts, etc., 3·94 g. The total yield was therefore 97·5%, the *p*-isomeride constituting 55% and the residues 45% of this isolated material. On oxidation by the customary method, nitrobenzoic acids (*M*, 166, 165, 166; benzoic acid, nil) were obtained in 89% yield, and this mixture contained 33% of *p*-nitrobenzoic acid (m. p. 230—235°) and 38% of *m*-nitrobenzoic acid (m. p. 120—135°, mixed m. p. 137—140°; after one crystallisation from ethyl acetate, m. p. 138—140°, mixed m. p. 139—140°). The original nitration product is therefore estimated to have contained: *para*, $55 + 0{\cdot}33 \times 45 = 70\%$; *meta*, $0{\cdot}38 \times 45 = 17\%$; *ortho* (by difference), 13%.

An artificial mixture of *p*-, *m*-, and *o*-picrates in the respective proportions, 68·4%, 19·9%, 11·7%, on oxidation gave a 97% yield of nitrobenzoic acids, which on separation gave 67·0% of *p*-acid, m. p. 233—234°, mixed m. p. 235°, and 19·1% of *m*-acid, m. p. 128—133°, mixed m. p. 136—139°.

(*i*) Another oxidation of the same mixture yielded 91% of mixed nitrobenzoic acids (*M*, 167, 168; benzoic acid, nil), and the mixture, on separation, was found to contain 24% of *p*-acid (m. p. 200—230°; mixed m. p. 225—235°) and 46% of *m*-acid (m. p. 115—130°; mixed m. p. 133—138°; m. p. after one crystallisation from ethyl acetate–ligroin, 137—140°). For the original nitration product this gives: *para*, 66%; *meta*, 21%; *ortho* (by difference) 13%. In view of the fact that in this and the previous experiment the mixed nitrobenzoic acids were obtained in only 90± 1% yield, these figures are regarded as rather less accurate than the others given in this paper.

(E) *Nitration of Trimethylbenzylammonium Picrate.*

For the sake of the numerical comparison on p. 250 this substance was prepared and nitrated under the conditions employed in example (D) and in the case of triethylbenzylammonium picrate (Goss, Ingold, and Wilson, *loc. cit.*), and the proportions of the isomerides were estimated. Ing and Robinson (*loc. cit.*) nitrated trimethylbenzylammonium nitrate and isolated 73·6% of pure *m*-derivative.

Benzyldimethylamine and trinitroanisole (1 mol.) were heated together in benzene solution at 70—75° for 0·5 hour, and the *trimethylbenzylammonium picrate* was collected and crystallised from alcohol, from which it separated in clusters of yellow prisms, m. p. 168—169° (Found: C, 51·2; H, 5·1. $C_{16}H_{18}O_7N_4$ requires C, 50·8; H, 4·8%).

The bulk of the nitration product was precipitated with gaseous ammonia (*loc. cit.*), the neutral filtrate evaporated to dryness, and the residue, after grinding with a little cold water, crystallised from boiling water. Total yield 93·6% (Found: C, 45·6; H, 3·7. $C_{16}H_{17}O_9N_5$ requires C, 45·4; H, 4·0%).

Separation.—The principle employed was that crystallisation from or extraction with concentrated alcohol favours the isolation of the *m*-compound, whilst in dilute alcohol or water this isomeride is relatively easily soluble. The well-ground and mixed nitration product (10·00 g.) was boiled with a large bulk of absolute alcohol, the solution filtered while still hot, and the residue crystallised from

50% alcohol (7·30 g. of meta, m. p. 179·5—180·5°). The aqueous-alcoholic solution was concentrated and alcohol was added (0·67 g. of meta, m. p. 179—180°), and the combined aqueous and alcoholic solutions were then evaporated to dryness and the residue was extracted with successive portions of hot absolute alcohol until the m. p. of the undissolved portion rose above 175°. This portion was then crystallised from 50% alcohol (0·42 g. of meta, m. p. 179—180°) and the filtrate was concentrated and mixed with alcohol as before (0·17 g. of meta, m. p. 178—179·5°). All liquors were now combined and evaporated and the residue was crystallised from water (0·23 g. of para, m. p. 193—194°), the filtrate being concentrated (0·12 g. of para, m. p. 192—194°) and mixed with alcohol (0·02 g. of meta, m. p. 178—179°). The totals separated are therefore : para 3·5%, meta 85·8% (total 89·3%). The mother-liquors were now distilled completely from a water-bath under slightly diminished pressure and the distillate was treated with sodium picrate prepared from 0·5 g. of picric acid, and with 0·67 g. of *m*-nitrobenzyltrimethylammonium picrate. The undissolved portion weighed 0·44 g., so that the saturated solution contained 0·23 g., and 0·62 g. of picrate ions. The quantity of picrate ions contained in the solution before the distillation was 0·59 g.

The residue from the distillation, on oxidation with 240 c.c. of 3% permanganate and 200 c.c. of water, gave 0·305 g. of acids, from which 0·201 g. of *p*-nitrobenzoic acid (m. p. 230—233°; mixed m. p. 232—234°) was obtained by digestion with chloroform (solubility correction, 0·026 g.), but the separation of *m*-nitrobenzoic acid through the barium salt was spoilt by the presence of oxalic acid. *p*-Nitrobenzyltrimethylammonium picrate (1·50 g.), on oxidation under the same conditions, gave 0·55 g. of *p*-nitrobenzoic acid (m. p. 234—235°)—that is, 90% of the theoretical—so that the *p*-nitrobenzoic acid isolated by oxidation of the residues may be taken to correspond with 0·64 g. of the *p*-picrate.

Hence, for the original nitration product, we have :

	Separation.	Solubility.	Oxidation.	Total.
Ortho-	—	—	—	—*
Meta-	85·8	2·3	—	88%
Para-	3·5	—	6·4	10 ,,

* The figure, 2%, obtained by difference is without significance.

For use in identifying the separated products, the *m*- and *p*-nitro-compounds were prepared from the appropriate tertiary base and trinitroanisole. m-*Nitrobenzyltrimethylammonium picrate* separates from water in pyramid-capped prisms or stout rhombs, m. p. 180—180·5° (Found : C, 45·7; H, 4·2. $C_{16}H_{17}O_9N_5$ requires

C, 45·4; H, 4·0%). It is very sparingly soluble in boiling methyl or ethyl alcohol. p-*Nitrobenzyltrimethylammonium picrate* separates from water or ethyl alcohol in fern-like aggregates of leaflets or flattened needles, m. p. 194° (Found: C, 45·8; H, 4·1%).

THE UNIVERSITY, LEEDS. [*Received, September 29th,* 1926.]

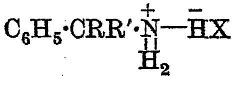
XLI.—*The Nature of the Alternating Effect in Carbon Chains. Part XI. Further Evidence on the Substitution of Benzylamine Salts.*

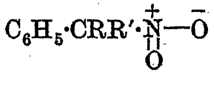
By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

IT has previously been suggested (Goss, Ingold, and Wilson, J., 1926, 2440) that the formation of comparatively large quantities of *m*-isomeride in the nitration of benzylamine salts arises from the action of the dipole contained in the salt grouping, which sets up electronic strain of a similar kind to that produced by the free charge in the corresponding ion (I; A = H); and in support of this view it has, *inter alia*, been shown (Baker and Ingold, J., 1926, 2462) that phenylnitromethane, a substance analogous to a benzylamine salt but containing a stable dipole (I; A = O), nitrates in the *m*-position to approximately the same extent as benzylamine itself.

$$\text{(I.)}\ C_6H_5 \rightleftarrows CH_2 \rightleftarrows \overset{+}{N}—\overset{-}{A}\left\{\begin{array}{l}\rightarrow \text{electron attraction towards } + \\ \leftarrow \text{partly compensating repulsion from } -.\end{array}\right.$$

Although this result was predicted from the analogous constitution of the two types, agreement in a single case may possibly be fortuitous, and it was therefore considered desirable to extend the comparison to a series of substituted benzylamines (II) and the corresponding phenylnitromethane derivatives (III) in order to ascertain if the agreement were general.

(II.)

$$C_6H_5\cdot CRR'\cdot\underset{H_2}{\overset{+}{N}}—\overset{-}{HX}$$


$$C_6H_5\cdot CRR'\cdot\underset{O}{\overset{+}{N}}—\overset{-}{O}$$
(III.)

The nitration of benzylamine itself (II; RR′ = H_2), of β-nitro-β-phenylpropane (III; RR′ = Me_2), and of phenylnitromethane (III; RR′ = H_2) had already been carried out, and in this paper the nitration of α-phenylethylamine (II; RR′ = MeH), α-phenyl*iso*propylamine (II; RR′ = Me_2), and α-nitro-α-phenylethane (III; RR′ = MeH) is described. The results obtained render possible a comparison between the three pairs of analogously constituted benzylamine and phenylnitromethane derivatives.

The proportion of *m*-isomeride formed in each case is indicated in the following table :

Type.	$RR' = H_2$.	$RR' = MeH$.	$RR' = Me_2$.	
$C_6H_5\cdot CRR'\cdot NH_3X$	49	40	26	% meta-derivative.*
$C_6H_5\cdot CRR'\cdot NO_2$	50	43	27	„ „ „ *

* Estimated from the weights of separated but unrecrystallised *m*-nitrobenzoic acid obtained after oxidation of the mixed isomerides (compare preceding paper).

In all three cases the anticipated agreement is found to exist.

EXPERIMENTAL.

In this section, only those details are recorded which could not be inferred from the experimental descriptions given in Parts VIII, IX, and X (J., 1926, 2440, 2462; preceding paper).

(i) *Nitration of α-Nitro-α-phenylethane.*—The nitro-compound (b. p. 126—130°/30 mm.), prepared as already described (Baker and Ingold, *loc. cit.*), was nitrated at −15° with nitric acid (d^{16° 1·49). The rate of addition of the nitro-derivative to the acid was 1·0 g. per hour, and the mixture was kept for a further 3·0 hours at −15——10° before being warmed to 0°; ice was then added. On being worked up as in the nitration of phenylnitromethane (*loc. cit.*), the nitration product (Found : C, 48·8; H, 4·6. Calc. : C, 48·6; H, 4·2%) was obtained; it crystallised almost completely, and a portion when drained had m. p. 80°. The total yield was 91%, and a further 3% of the material was accounted for as acid by-products. The whole nitration product, on oxidation by permanganate, gave mixed nitrobenzoic acids (Found : C, 50·4; H, 3·6. Calc. : C, 50·3; H, 3·0%) in 96% yield. The separated *p*-nitrobenzoic acid (34%) had m. p. 228° (mixed m. p. 231°). The separated *m*-nitrobenzoic acid (43%) was collected in two portions, one, the major portion (precipitated), having m. p. 136° (mixed m. p. 141°), and the second (extracted with ether) having m. p. 123° (mixed m. p. 134—135°).

(ii) *Nitration of α-Phenylethylamine.*—α-Phenylethylamine (10 g.) was nitrated with nitric acid (60 g.; d^{16° 1·50) at −10°. The addition occupied 3·5 hours, and the product was kept at −10° for a further 1·5 hours, warmed to 0° during 1·5 hours, and mixed with ice. After the extraction of neutral and acid by-products with ether, the nitro-bases were liberated by addition of sodium hydroxide and extracted with ether, and then re-extracted from the ethereal solution with dilute hydrochloric acid. The yield of hydrochlorides was 89% (Found : Cl, 17·7. Calc. : Cl, 17·5%). Oxidation by permanganate gave nitrobenzoic acids in a yield of 89% (Found : *M*, 167; benzoic acid, by sublimation, nil).

The separated *p*-nitrobenzoic acid (56%) had m. p. 229° (mixed m. p. 233—234°), and the *m*-acid (38%) m. p. 133° (mixed m. p. 139°).

The mixed hydrochlorides were converted into picrates and these were crystallised from 50% methyl alcohol. The crystallised portion (64%, m. p. 190—205°), on oxidation with permanganate, gave nitrobenzoic acids (Found : *M*, 168 ; benzoic acid, nil) in 85% yield. On separation, the *p*-acid (75%) had m. p. 234—235° (mixed m. p. 234—235°) and the *m*-acid (20%) had m. p. 131—137° (mixed m. p. 138—140°). The mother-liquor from the crystallisation of the picrates was evaporated with water to remove the methyl alcohol and oxidised; nitrobenzoic acids were then isolated in 82% yield (Found : *M*, 166; benzoic acid, 1·1%). The separated *p*-acid (17%) had m. p. 230—234° (mixed m. p. 232—235°), and the *m*-acid (78%) m. p. 129—136° (mixed m. p. 137—140°). After one crystallisation from ethyl acetate–ligroin, the latter melted at 140°. Combining the results obtained with these two picrate fractions, the original nitration product is estimated to have contained : para, $0{\cdot}17 \times 36 + 0{\cdot}75 \times 64 = 54\%$; meta, $0{\cdot}78 \times 36 + 0{\cdot}20 \times 64 = 41\%$. The mean of the two determinations gives *para* 55%, *meta* 40%.

(iii) *Nitration of α-Phenyl*iso*propylamine.*—This base was prepared according to the scheme $CH_2Ph{\cdot}CN \longrightarrow CMeHPh{\cdot}CN \longrightarrow CMe_2Ph{\cdot}CN \longrightarrow CMe_2Ph{\cdot}CO{\cdot}NH_2 \longrightarrow CMe_2Ph{\cdot}NH_2$, Haller and Bauer's procedure (*Ann. Chim. Phys.*, 1918, **9**, 8) being followed in the first three stages. The last stage has been effected by Brander (*Rec. trav. chim.*, 1918, **37**, 67), who, however, records no detailed directions. Bromine (27 g.) and the amide (27 g.) were successively added to a solution of potassium hydroxide (9·5 g.) in water (90 c.c.), and the yellow suspension thus formed was gradually added with cooling to a solution of potassium hydroxide (28·5 g.) in water (300 c.c.). After heating on the water-bath for 1 hour, the mixture was cooled and extracted with ether, and the base was extracted from the ether with aqueous hydrochloric acid, liberated by the addition of alkali, and then re-extracted with ether. It had b. p. 94—95°/22 mm., and the hydrochloride had m. p. 240° (decomp.) (Found : Cl, 20·7. Calc. : Cl, 20·7%). The same base was also obtained in small yield by reduction of β-nitro-β-phenylpropane, as described by Konovalov (*J. Russ. Phys. Chem. Soc.*, 1894, **26**, 68); the hydrochloride obtained in this way had the same m. p., and a mixture with the other specimen showed no m. p. depression (Konovalov records m. p. 235·5°).

Nitration was effected at —10° with nitric acid ($d^{16°}$ 1·49), the speed of addition being 1·1 g. per hour. The product was kept for a further 3 hours at about $-10°$ and for 0·3 hour at 0°; ice was then added and the mixed nitro-bases were isolated as hydrochlorides. The yield was 95% (Found: Cl, 16·4. Calc.: Cl, 16·4%), and a further 2% of the material used was obtained as acid by-product, evidently formed by oxidation. The mixed chlorides, on oxidation with nitric acid, gave nitrobenzoic acids in 82% yield (Found: M, 165·5; benzoic acid, nil). The separated *p*-acid (58%) had m. p. 233—235° and the mixed m. p. was 234—235°. The *m*-acid was collected in two portions; one (precipitated; yield 19%) had m. p. 138—139°, the mixed m. p. being 140°, whilst the other (extracted; 8%) had m. p. 129—134° (mixed m. p. 137—139°), and on crystallisation from ethyl acetate–ligroin had m. p. 139—140°. The total *m*-acid was therefore 27%.

The mixed hydrochlorides (2·00 g.) were converted into picrates, which crystallised from 300 c.c. of boiling water in bunches of sulphur-yellow needles, m. p. 230° (1·68 g.). These, on crystallisation from 125 c.c. of boiling water, yielded 1·51 g. (40%) of crystals, m. p. 234°, and further crystallisation did not alter this m. p. This compound appears to be α-p-*nitrophenyl*iso*propylammonium picrate* (Found: C, 44·5; H, 3·7. $C_{15}H_{15}O_9N_5$ requires C, 44·0; H, 3·7%), since oxidation of the corresponding nitrate with nitric acid gave *p*-nitrobenzoic acid, m. p. 230—233°, mixed m. p. 232—235°, in 86% yield. The combined mother-liquors, containing 60% of the original mixed picrates, were worked up for nitro-bases and these were oxidised; an 81% yield of nitrobenzoic acids was then obtained (Found: M, 168; benzoic acid, nil). The separated *p*-nitrobenzoic acid (33%) had m. p. 225—232°, mixed m. p. 229—234°; the *m*-acid was isolated in two portions, one (precipitated) having m. p. 136—139°, mixed m. p. 139—140° (32%), and the other (extracted from solution with ether) having m. p. 126—132°, mixed m. p. 136—140° (10%). The latter portion, after a single crystallisation from ethyl acetate–ligroin, had m. p. 140°. The original mixture of picrates is therefore estimated to have contained: para, $40 + 0·33 \times 60 = 60\%$; meta, $0·42 \times 60 = 25\%$. The mean of the two determinations gives *para*, 59%; *meta*, 26%.

We desire to thank the Royal Society for defraying part of the expense of this research.

THE UNIVERSITY, LEEDS. [*Received, September 29th,* 1926.]

XLII.—*The "Uniform Movement" of Flame in Mixtures of Hydrogen and Air.*

By ELIZABETH HELEN MACLEOD GEORGESON and
FRANCIS JOHN HARTWELL.

THE measurement of the speed of the so-called "uniform movement"* of flame in gaseous mixtures has been found to be of considerable value as affording an indication of the relative rates of inflammation of different mixtures. The earlier methods of measuring this speed, which is not great in the majority of mixtures of inflammable gases with air, have usually depended upon the electrical registration of the time of fusion of fine screen-wires stretched at measured intervals across the tube in which the flame travels. This "screen-wire" method of measurement, although sufficiently accurate in experienced hands, is clearly not to be compared as regards general usefulness with the photographic method of analysing the movement of flames, using a rapidly revolving drum, which Professor H. B. Dixon has developed; for the latter method enables any slight variations in the speed of the flame from point to point along the tube to be detected, and ensures that if, as in the present instance, the speed of the uniform movement alone is required, no other phase in the propagation of flame (such as the "vibratory movement" which immediately succeeds the uniform movement) shall be included in the measurements, a matter which is sometimes by no means easy to arrange when the screen-wire method is used.

In connexion with other researches that are being carried out in these laboratories, it became necessary to obtain strictly comparable measurements of the speed of uniform movement of flame in mixtures of different inflammable gases (including hydrogen) with air, and it was decided to use the photographic method throughout. Photographic registration of the feebly actinic flames during the uniform movement in hydrogen–air mixture has presented considerable difficulty, but we have recently succeeded in obtaining satisfactory records, over a fairly wide range of mixtures, by using a tube of transparent quartz and photographing the flames through a quartz lens on Lumière bromide paper of special sensitivity. The outside of the tube was partly covered with black paper, leaving a horizontal slit 7 mm. wide throughout its length.

The quartz tube, which was 90 cm. long and of 2·4 cm. internal diameter, was supported horizontally and, as a precaution in the event of the detonation-wave being set up, was attached to a straight extension piece of lead piping, closed at the far end. The open end of the tube was provided with a flange, and a flanged cover, fitted with a tubulure and tap for the introduction of the explosive mixture, could be clipped thereto (see J., 1914, **105**, 2609). This cover was removed by gently sliding it upwards just before igniting the mixture, which was effected by passing a large flame comparatively slowly across the now open end of the tube. In this way, mechanical disturbance of the mixture at the moment of ignition was avoided and the mixture was ignited exactly at the open end. Unless these precautions were taken, and the same procedure adhered to rigidly, it was found that the "uniform movement" was not maintained over an appreciable distance of travel of the flame, or varied in speed from one experiment to another with a mixture of the same composition. Although precautions of the character described are required with all inflammable mixtures if accurate results are to be obtained, the uniform movement in mixtures of hydrogen and air seems to be particularly sensitive to extraneous disturbances.

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* The uniform movement occurs when the inflammable mixture is contained in a horizontal tube, closed at one end and open at the other, and is ignited at the open end. It is usually maintained over about one-third of the length of the tube.

Photographs were successfully obtained of the flames moving in mixtures containing between 20 and 50% of hydrogen. On either side of this range the records were too faint to measure. With each mixture three photographs were taken of successive lengths of 26 cm. of the tube, whence a composite photograph, showing the flame as it travelled from the open end over a distance of 79·5 cm. towards the closed end, was obtained. Typical photographs, reduced in size for reproduction, are shown on Plate I.

On close analysis of the movement of the flame, it was found that, in each mixture, its speed fluctuated during the first 26 cm. of travel, remained reasonably uniform over the next 26 cm.,* and then decreased slightly, antecedent to the vibratory movement, within the next 26 cm. We have therefore recorded, as the speed of "uniform movement" in the mixture concerned, that obtaining over the distance 29—55 cm. measured from the open end of the tube. Typical photographs of flames travelling in different mixtures over this section of the tube are reproduced in Plate II. The general results are recorded in Table I.

Apart from the anomalous results obtained with the 23·9 and 24·95% mixtures, which we are unable completely to explain,†

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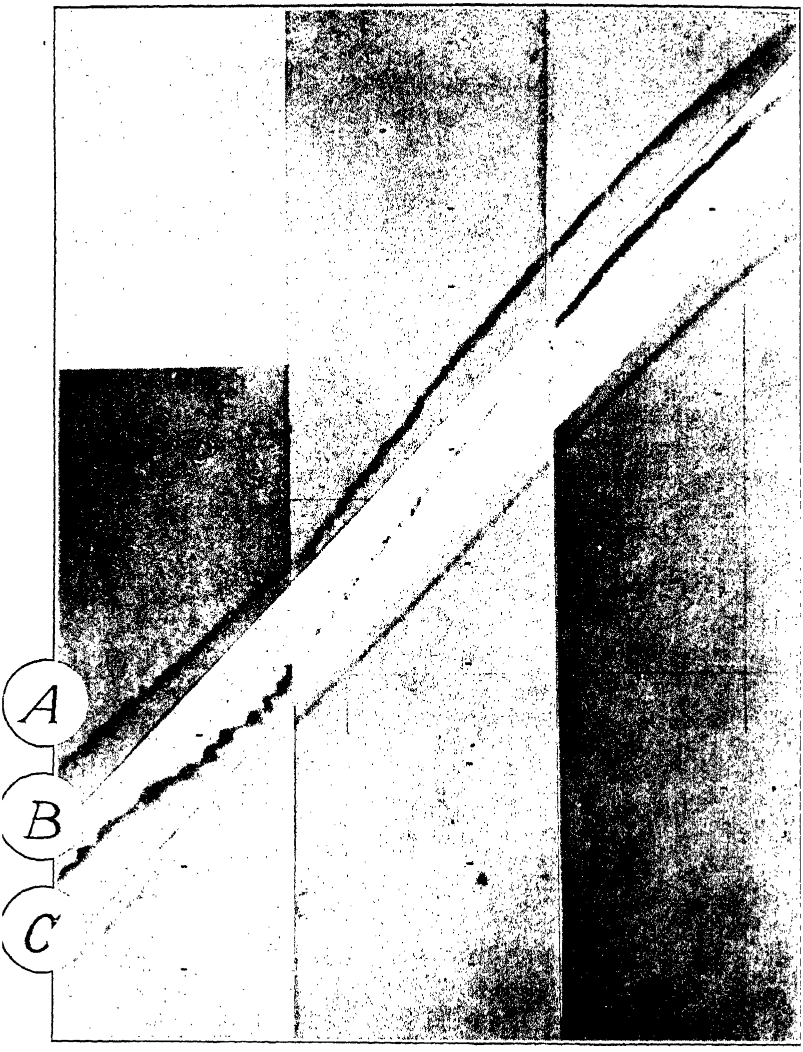
* Faint undulations that made their appearance during this period did not affect the mean speed of the flame.

† The vibratory movement apparently started earlier with these mixtures than with the others.

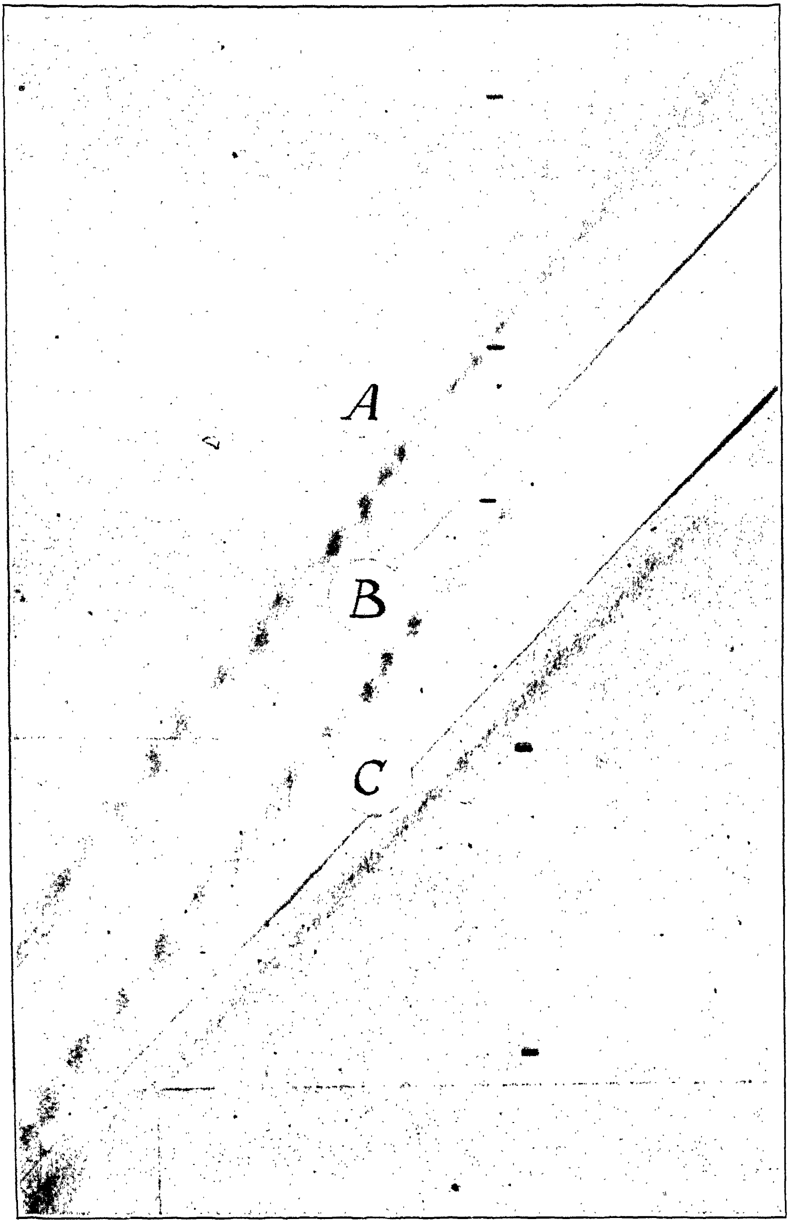
PLATE I.



The propagation of flame in mixtures of hydrogen and air.
A. 26·95%. B. 30·95%. C. 41·70%.

[*To face p.* 266.]

PLATE II.



The uniform movement of flame in mixtures of hydrogen and air.
A. 26·95%. B. 30·95%. C. 41·70%.

TABLE I.

The Uniform Movement of Flame in Mixtures of Hydrogen and Air.
(Tube 2·4 cm. in diameter.)

Comp. of mixture (hydrogen %).	Speed of uniform movement (cm. per sec.).	Comp. of mixture (hydrogen %).	Speed of uniform movement (cm. per sec.).
20·30	320, 323	36·70	474, 464
23·90	437, 414	37·50	520
24·95	462	40·45	478, 472
26·95	371, 362	41·70	501, 493
30·95	424, 418	45·45	433, 434
33·30	462, 461, 436	49·65	395, 393
34·90	501, 491		

these figures are comparable with those recorded by Haward and Otagawa (J., 1916, **109**, 83), when using a glass tube of 2·5 cm. internal diameter and measuring the mean speeds of the flames over the distance 10—50 cm., from the open end, by the screen-wire method.

A future communication will deal with the speed of the uniform movement in hydrogen mixtures in which the nitrogen of the air has been replaced by either argon or helium. A striking feature of the results is the high actinic value of the flames.

This work has been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD.
[*Received, October 15th, 1926.*]

XLIII.—*The Normal Oxidation–Reduction Potential of Mercury.*

By SYDNEY RAYMOND CARTER and ROBERT ROBINSON.

THE normal oxidation potential of mercury has hitherto only been obtained by indirect methods, since most of the mercuric or mercurous salts suffer from one or more of the disadvantages of low solubility, small degree of ionisation, and a tendency towards the formation of complex salts and ions.

An examination of the mercurous and mercuric perchlorates shows that these salts are practically free from the above objections, and as they can be prepared in a state of purity they are suitable for a direct determination of this potential.

Preparation of Perchlorates.

Mercuric perchlorate was prepared according to Chikashigé (J., 1895, 67, 1013): a slight excess of red mercuric oxide was ground up with 2*N*-perchloric acid and, after filtration through asbestos, the solution was concentrated at 40—50° under reduced pressure until crystals separated. Evaporation under reduced pressure appeared to inhibit the formation of basic perchlorates. The crystals were recrystallised from water by a similar evaporation and then dissolved in water, giving a solution in which $[Hg(ClO_4)_2] = 0{\cdot}0922N$, the mercury being determined by precipitation with hydrogen sulphide. In preparing the solution of mercuric perchlorate for the second series of determinations, the salt was not isolated, the heated and filtered solution being diluted suitably.

Mercurous perchlorate was prepared (Linhart, *J. Amer. Chem. Soc.*, 1916, 38, 2358) by treating perchloric acid with a slight excess of mercurous oxide, in contact with mercury. After standing for some time, the solution was filtered and allowed to remain in contact with mercury for several days. By precipitation with potassium chloride, it was found that $[Hg_2(ClO_4)_2] = 0{\cdot}080N$. The solution also contained a small amount of mercuric perchlorate equal to 0·0148*N*. In preparing the solution of mercurous perchlorate for the second series of experiments, mercuric perchlorate was reduced with mercury; reduction was not complete, the resulting solution containing a mixture of mercurous and mercuric perchlorates.

To check the purity of the solution of mercurous perchlorate, it was diluted to a strength of $0{\cdot}1N\text{-}\frac{1}{2}Hg_2(ClO_4)_2$, and the following cell constructed:

$$Hg|0{\cdot}1N\text{-}\tfrac{1}{2}Hg_2(ClO_4)_2|0{\cdot}1N\text{-}KNO_3|N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg.$$

It was found to have a potential of 0·4720 and 0·4718 volt on two successive days. For a similar cell, Ley and Heimbucher (*Z. Elektrochem.*, 1904, 10, 301) found the potential 0·4719 volt.

Construction of Cells.

The oxidation element consisted of about 100 c.c. of a solution prepared by mixing the above two solutions in the requisite proportions. Three electrodes of bright, unplatinised platinum foil were used, about 1 sq. cm. in area. The complete cell was:

$$Pt|Hg(ClO_4)_2,\ Hg_2(ClO_4)_2\underset{a}{|}0{\cdot}1N\text{-}KNO_3\underset{b}{|}N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg.$$

The connecting syphon tubes at *a* and *b* were filled with the solution of the oxidation element and with *N*-KCl, respectively. The three electrodes gave perfect agreement between themselves, and the potential was constant over several days. The cells could be reproduced with a variation of about 0·3 millivolt. After measuring the potential, the cell solution was analysed, mercurous mercury being estimated as calomel, whilst the mercuric mercury in the filtrate was determined as sulphide. All measurements were made at 18°; potentials were referred to the absolute scale and were given a positive sign if the current flowed through the cell from the normal calomel electrode.

The diffusion potentials at *a* and *b* have been shown by Ley and Heimbucher (*loc. cit.*) to be of a small order (less than 1 milllivolt), and have been neglected in this investigation.

Deduction of the Normal Oxidation Potential.

The behaviour of the system is determined by the equation:

$$E = E_0 + 0{\cdot}029 \log [Hg^{\cdot\cdot}]^2/[Hg_2^{\cdot\cdot}] \quad . \quad . \quad . \quad . \quad (1)$$

E_0 being the normal oxidation potential and E the potential of the half-element corresponding to the given mercurous- and mercuric-ion concentrations. Now if α_1 and α_2 are the degrees of dissociation of the mercuric and mercurous perchlorates, respectively, then

$$E = E_0 + 0{\cdot}029 \log \alpha_1^2[Hg(ClO_4)_2]^2/\alpha_2[Hg_2(ClO_4)_2] \quad . \quad . \quad (2)$$

which may be written:

$$E = E_0 + 0{\cdot}029 \log [Hg(ClO_4)_2]^2/[Hg_2(ClO_4)_2] + 0{\cdot}029 \log \alpha_1^2/\alpha_2 \quad (3).$$

The last term introduces a small correction, due to the incomplete dissociation of the perchlorates. Hence, if the potential of the half-element is known, and also the concentrations of the mercurous and mercuric perchlorates, then, by substitution in equation (3), E_0, the normal oxidation potential, may be calculated.

Correction for Incomplete Dissociation of the Perchlorates.—In order to obtain α_1 and α_2, the degrees of dissociation of the mercury perchlorates, we have assumed that these salts are dissociated to the same extent as barium perchlorate. This is based on a consideration of the conductivity–dilution curves and hydrolysis data for barium, mercurous, and mercuric perchlorates, which have been determined by Ley and Heimbucher (Diss., Würzburg, 1904). A solution used in these cells (with the exception of cell No. 3) may be considered as being made by the admixture in suitable proportions of two separate solutions, one of mercurous and the other of mercuric perchlorate, the concentration of each being equal to the total salt concentration in the cell; such solutions will be "isoionic" with one another, *i.e.*, the extent of dissociation of the original solutions will not be affected on mixing. Hence by taking the degree of dissociation of barium perchlorate for the total salt concentration, since $\alpha_1 = \alpha_2$, we can determine $0{\cdot}029\log\alpha_1{}^2/\alpha_2$ for each cell solution.

Moreover, Ley and Heimbucher have shown that mercurous perchlorate is hydrolysed to the extent of 3—4% in these solutions; and we have shown that mercuric perchlorate is hydrolysed to a similar extent (3%) in 0·05*N* solution. Hence the correction to be applied is $0{\cdot}029\log(0{\cdot}97\alpha_1)^2/(0{\cdot}97\alpha_2)$ or $0{\cdot}029\log(0{\cdot}97\alpha_1)$. Now in the solutions that we have studied, $\alpha_1 = 0{\cdot}73$, hence the correction is — 0·0044 volt. It will be seen that the effects of hydrolysis of the perchlorates are of a small order and almost negligible.

Results.

Table I summarises the measurements of nine cells. The observed *E.M.F.*, E_c, of the whole cell is given in col. 7. From this value, the normal oxidation potential E_0 (col. 8) is deduced by substituting the logarithmic correction term (col. 6) in equation (2) and adding the potential of the calomel electrode, 0·560 volt.

TABLE I.

$m = [Hg(ClO_4)_2]$, $n = [Hg_2(ClO_4)_2]$.

Cell No.	m.	n.	m/n.	m^2/n.	$0{\cdot}029\log m^2/n$.	E_c.	E_0.
1	0·0493	0·0431	1·144	0·0564	−0·0407	0·5885	1·1892
2	0·0493	0·0431	1·144	0·0564	−0·0407	0·5882	1·1889
3	0·0049	0·00417	1·175	0·00576	−0·0694	0·5569	1·1863
4	0·0236	0·0670	0·352	0·00831	−0·0647	0·5634	1·1890
5	0·0160	0·0770	0·208	0·00333	−0·0763	0·5540	1·1903
6	0·0121	0·0722	0·168	0·00203	−0·0825	0·5489	1·1914
7	0·0199	0·0707	0·282	0·00561	−0·0697	0·5607	1·1904
8	0·0560	0·0539	1·039	0·05818	−0·0404	0·5902	1·1906
9	0·0581	0·0609	0·954	0·05543	−0·0409	0·5907	1·1916

The results may be divided into two series, since the later cells (Nos. 7, 8, and 9) were made up from slightly different solutions, as previously indicated (see "Preparation of Perchlorates").

Cell No. 3 was a much more dilute solution, having been prepared by ten-fold dilution of Cell No. 1. In this case, hydrolysis of the mercuric perchlorate is considerable (about 15%), and is probably sufficient to account for the low value of E_0.

The mean *E.M.F.* of these cells (with the exception of Cell No. 3) is 1·1902 volt, with an average error of ± 0·0008 volt.

The Effect of Perchloric Acid on the Potential.—To determine this, four cells were constructed, by mixing 50 c.c. of a solution in which $[Hg(ClO_4)_2] = 0{\cdot}0687N$ and $[Hg_2(ClO_4)_2] = 0{\cdot}0396N$, with the calculated quantity of 2*N*-perchloric acid and sufficient water to make the total volume up to 100 c.c. The following potentials were observed :

TABLE II.

Cell No.	10.	11.	12.	13.
$[HClO_4]$	1*N*	0·5*N*	0·1*N*	Nil.
E.M.F. (obs.)	0·5390	0·5443	0·5728	0·5915

The addition of free perchloric acid to the solution decreases the extent of dissociation of both the perchlorates of mercury, the decrease in the case of the mercuric salt being the predominating factor, because the square of this concentration and only the first power of the mercurous salt concentration enters into equation (2). Thus the observed *E.M.F.* is diminished by addition of perchloric acid. Quantitatively the effect may be expressed thus: substituting the values $[Hg^{\cdot\cdot}] = K_1[Hg(ClO_4)_2]/[ClO_4']^2$ and $[Hg_2^{\cdot\cdot}] = K_2[Hg_2(ClO_4)_2]/[ClO_4']^2$ equation (1) becomes

$$E = E_0 + 0{\cdot}029 \log K_1^2[Hg(ClO_4)_2]^2/K_2[Hg_2(ClO_4)_2][ClO'_4]^2.$$

Since $[Hg(ClO_4)_2]$ and $[Hg_2(ClO_4)_2]$ are constant in the four cells of Table II, these quantities, together with K_1, K_2, and E_0, have been incorporated in a fresh symbol E'_0, and, therefore,

$$E = E'_0 - 0{\cdot}058 \log [ClO_4'].$$

Assuming complete dissociation of both the mercury salts and of the perchloric acid, and taking *E.M.F.* (obs.) = 0·5915 (Cell 13) as a starting point for *E.M.F.* (calc.), the following values of the potentials are calculated:

TABLE III.

Cell No.	10.	11.	12.	13.
$[ClO_4']$	1·11	0·61	0·21	0·11
E.M.F. (obs.)	0·5390	0·5443	0·5728	0·5915
E.M.F. (calc.)	0·5333	0·5483	0·5753	(0·5915)

It is evident that the variation of the potential with perchloric acid concentration can be accounted for satisfactorily, and it is therefore probable that complex-ion formation between the free acid and the salts is either absent or negligible.

It was necessary to show that the potentials measured in this investigation were not due to the perchlorate radical. Experiments were therefore carried out with a platinum-foil electrode dipping into solutions of *N*-perchloric acid and 0·1*N*-potassium perchlorate, respectively. The potentials obtained were ill-defined and in no way resembled those registered in the case of the mercury salts.

Comparison with Previous Data on the Normal Oxidation Potential.

The present investigation gives a value of $E_0 = + 1{\cdot}190$ volts on the absolute scale, or ${}_0E_h = + 0{\cdot}913$ volt on the hydrogen scale.

The value given in Abegg's "Handbuch der Anorganischen Chemie," [1905, II, (2), 561] is ${}_0E_h = 0{\cdot}87$, obtained by calculation from the normal electrode potential Hg—$Hg_2^{\cdot\cdot}$, ${}_0E_h = 0{\cdot}75$ volt, and the equilibrium relations in the system Hg—$Hg_2^{\cdot\cdot}$—$Hg^{\cdot\cdot}$, in which the ratio $[Hg^{\cdot\cdot}]/[Hg_2^{\cdot\cdot}] = 235$. This value, 0·87 volt, is probably low, since later determinations of the potential Hg—$Hg_2^{\cdot\cdot}$ (${}_0E_h = 0{\cdot}75$) give a somewhat higher figure; thus Lewis and Randall ("Thermodynamics," 1923, 419) give ${}_0E_h = 0{\cdot}7986$, based on Linhart's measurements, and Abegg, Auerbach, and Luther ("Messungen elektromotorischer Kräfte galvanischer Ketten," 1915, 46) give ${}_0E_h = 0{\cdot}80$. The latter authors have given a value of the normal oxidation potential $2Hg^{\cdot\cdot}$—$Hg_2^{\cdot\cdot}$, ${}_0E_h = 0{\cdot}92$, which is in good agreement with our experimental results.

Conclusions.

Mercurous and mercuric perchlorates have been prepared and found to be suitable for electrochemical measurements, as their solutions are capable of registering steady potentials with platinum electrodes.

The normal oxidation potential of the process $2Hg^{\cdot\cdot}$—$Hg_2^{\cdot\cdot}$ is $+ 1{\cdot}190$ volts.

The effect of free perchloric acid on the potential has been investigated.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of them (R. R.) which has enabled him to participate in this investigation.

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[*Received, November* 10*th*, 1926.]

XLIV.—*The Adsorption of Benzene Vapour on the Plane Surfaces of Glass, Fused Quartz, and Platinum. The Isosteric Heat of Adsorption of Benzene on Platinum.*

By SAM LENHER.

IT has been previously shown that water vapour is strongly adsorbed on various surfaces at pressures above 95% of saturation (McHaffie and Lenher, J., 1925, **127**, 1559; Lenher, J., 1926, 1785).

The method of measuring the adsorption of benzene on the several surfaces is that described in the above two papers. It consists in obtaining measurements of the change of pressure with temperature of a vapour at constant volume, using the inside surface of the constant-volume vessel as the adsorbing surface. The following modification was, however, made in the apparatus: the bulb containing the benzene was placed outside the thermostat and a mercury-sealed vacuum-tight tap was used to close it from the apparatus instead of a mercury trap as before.

In all experiments, the adsorption vessel was baked out in a high vacuum immediately before each determination. A furnace consisting of a copper tube wound with nichrome wire and asbestos sheeting was slipped over the adsorption chamber and fixed in position so that the entire tube from the top to the tip of the pointer could be uniformly heated. The furnace was slowly brought to the maximum temperature, which was maintained for 2—3 hours while the vessel was constantly evacuated to 1×10^{-6} cm. The experiment was then begun as soon as the tube had cooled to room temperature.

The benzene used was Kahlbaum's "thiophene-frei" brand. After a thorough drying over phosphorus pentoxide, the benzene was tested for thiophen and gave a negative result. The benzene was distilled after being frozen out twice, the fraction passing over from 80·15—80·20° (standard thermometer) being used. Determinations of the vapour pressure of this benzene gave results agreeing well with those of Dejardin (*Ann. Physique*, 1919, **11**, 253). The saturation pressures determined experimentally agreed excellently with values of the pressure calculated from Dejardin's equation for the vapour pressure of benzene at temperature t, $\log p = 0{\cdot}87476 + 0{\cdot}020670(t - 20) - 755 \times 10^{-7}(t - 20)^2 + 16{\cdot}5 \times 10^{-8}(t - 20)^3$.

The mercury-sealed tap between the bulb of benzene and the adsorption apparatus, and the tap between the vacuum pumps and the adsorption apparatus in the thermostat, were lubricated with metaphosphoric acid prepared by the method of Chapman and Gee (J., 1911, **99**, 1726). In the experiments with a silica vessel, the glass–silica ground joint was lubricated with phosphoric acid before sealing with mercury. The glass, quartz, and platinum adsorption tubes were those used in the earlier parts of this research.

The Adsorption of Benzene Vapour on a Glass and on a Fused Quartz Surface.

Before each experiment, the glass tube was baked out at 250° for 3 hours in high vacuum. Every experiment was done in its entirety at least twice, once from the side of increasing temperature and once from the side of decreasing temperature, to test the complete reversibility of the adsorption equilibrium. This applies also to the experiments with silica and platinum.

In calculating the number of molecules adsorbed per sq. cm. of surface the equation is the same as that used in the calculations on the adsorption of water on glass, $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 2{\cdot}344 \times 10^{18}$. To express the adsorption in terms of the number of molecular layers (θ), the size of the benzene molecule must be known. Various workers (Jeans, "Dynamical Theory of Gases," 1921; Eucken, *Physikal. Z.*, 1913, **14**, 331; Mack, *J. Amer. Chem. Soc.*, 1925, **47**, 2468; Huggins, *ibid.*, 1922, **44**, 1607; 1923, **45**, 264) give values for the molecular diameter, and $5{\cdot}9 \times 10^{-8}$ cm. has been taken as a probable figure for the mean diameter. Using the square of this value as the area occupied by a single benzene molecule on the surface, the equation from which the number of layers of benzene molecules adsorbed has been calculated becomes $\theta = (p/T - p_1/T_1) \times 8{\cdot}158 \times 10^3$. All the calculations are based on the assumption of a solid surface, plane with respect to irregularities or interstices which would introduce capillary effects of the type considered by Patrick.

As before, the decrease of free energy, $-\Delta F$, of the benzene between the liquid state and that in an adsorbed film is calculated from the usual equation, $-\Delta F = RT \log p/p_1$. The results obtained from five experiments measuring the adsorption of benzene on a glass surface are summarised in Table I. The equilibrium pressures are given in mm. of mercury at 0°:

TABLE I.

Benzene–Glass.

		No. 1.					No. 1.		
T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.	T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.
293·9°	78·06	70·30	24·4	0·0	294·8°	79·09	7·03	2·4	18·4
294·0	78·30	51·56	17·9	2·0	295·0	79·23			
294·2	78·57	35·16	12·2	5·6	296·0	79·49			
294·4	78·76	23·44	8·1	9·7	298·0	80·16			
294·6	78·96	14·06	4·8	13·8	300·0	80·88			
		No. 3.					No. 6.		
298·2	95·30	56·25	19·6	0·0	301·1	108·70	56·25	19·6	0·0
298·4	95·63	36·16	12·2	4·8	301·2	109·00	35·16	12·2	3·3
298·6	95·83	23·40	8·1	9·0	301·4	109·24	23·44	8·1	7·6
298·8	96·01	16·41	5·7	13·7	301·6	109·44	11·71	4·1	13·4
299·0	96·18				301·8	109·63			
300·0	96·77				302·0	109·75			
302·0	97·50				303·0	110·20			
					305·0	111·05			
		No. 5.					No. 7.		
299·7	102·23	60·94	21·2	0·0	302·7	116·74	56·25	19·6	0·0
299·8	102·47	44·53	15·5	1·8	302·8	116·98	39·84	13·8	3·2
300·0	102·75	28·12	9·8	5·6	303·0	117·37	14·06	4·9	6·4
300·2	103·00	14·07	4·9	9·9	303·2	117·59	4·68	1·6	10·3
300·5	103·21	7·03	2·4	17·1	303·5	117·74			
301·0	103·48				304·0	118·09			
303·0	104·33				306·0	118·99			
304·0	104·81								

The results show that the equilibrium film which will just exert the saturated vapour pressure of benzene remains of practically constant thickness over the temperature range. The first reading in each series gives the data for this equilibrium film at the saturation pressure. The very low values for the decrease in free energy of the benzene on undergoing adsorption show how little affinity there is between benzene vapour and a glass surface. The data show that adsorption of benzene is measurable only over a temperature range of 0·8° from the saturation temperature, and that the equilibrium pressures of the loosely-held benzene films are practically the saturated vapour pressures. For comparison of these data with other adsorption work, one should consider the figures for the number of molecules adsorbed per sq. cm., for the apparently high values of θ are apt to be misleading, the large results being due to the size of the benzene molecule itself and not to a relatively great adsorption.

The quartz vessel was baked out at 500° for 2 hours in a high vacuum before each experiment. The amount of adsorption was found by use of the equations $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}395 \times 10^{18}$, and $\theta = (p/T - p_1/T_1) \times 1{\cdot}252 \times 10^4$. The data of five experiments measuring the adsorption of benzene vapour on a pure silica surface are given in Table II.

TABLE II.

Benzene–Silica.

		No. 1.					No. 3.		
T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.	T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.
292·0°	71·46	93·48	32·5	0·0	295·3°	83·25	68·21	23·8	0·0
292·2	71·73	64·73	22·5	3·6	295·4	83·61	28·76	10·0	2·7
292·5	72·14	25·16	8·7	8·4	295·6	83·80	14·38	5·0	6·4
292·8	72·37	7·19	2·5	14·9	295·8	84·00			
293·0	72·46				296·0	84·04			
294·0	72·75				298·0	84·94			
296·0	73·23								
		No. 2.					No. 4.		
294·0	78·67	71·90	25·0	0·0	297·8	93·62	64·73	22·5	0·0
294·2	78·95	43·14	15·0	2·8	298·0	93·98	28·76	10·0	4·2
294·4	79·20	21·57	7·5	6·4	298·5	94·38			
294·6	79·44				299·0	94·55			
294·8	79·51				300·0	94·98			
295·0	79·56				301·0	95·30			
297·0	80·11								
							No. 5.		
					301·6	111·44	61·11	21·2	0·0
					301·7	111·73	32·35	11·2	0·8
					302·0	111·92	21·57	7·5	8·1
					304·0	112·84			
					306·0	113·52			

These experiments show that the amount of adsorption decreases as the pressure and temperature are increased. This means that the temperature coefficient of desorption is greater than the pressure coefficient of adsorption. The magnitude of the adsorption of benzene on quartz is seen to be almost identical with the measured values for the adsorption on glass (Table I). This is to be expected, for the unsaturated surface forces from glass and from pure silica must be essentially the same as regards their strength in attracting and adsorbing such an indifferent vapour as that of benzene.

The test applied previously of allowing the apparatus to stand at constant temperature (such that adsorption is taking place) for 24 hours or longer, to determine if the equilibrium set up was a stable one, was applied repeatedly in the above experiments. In one experiment (Table II, No. 5), the apparatus was allowed to stand at constant temperature for 4 days; the pressure read at the end of this period was within 0·02 mm. of the initial reading. The equilibrium set up is therefore stable, and over a period of many hours there is no tendency for benzene to penetrate into the bulk of the solid.

The Adsorption of Benzene Vapour on Platinum.

The platinum adsorption tube was made by Messrs. Johnson, Matthey and Co. from burnished seamless platinum tubing. The rounded top end of the tube (see McHaffie and Lenher, *loc. cit.*, p. 1561) was closed by hammering the tube while hot. Before the constricted bottom end was added, the inside of the tube was given a high polish with rouge and chamois. When the narrow bottom end was put on, the tube was filled with rosin to protect the polished surface. After the smaller connecting tube had been worked on to the main adsorption vessel and the rosin had been removed, the inside surface was given a light polish and was carefully cleaned chemically before use.

The equations giving the adsorption are $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}359 \times 10^{18}$ and $\theta = (p/T - p_1/T_1) \times 1{\cdot}169 \times 10^4$. The tube was baked out at 300° for 2 hours in a high vacuum before each experiment. Table III gives a few of the results of 12 experiments measuring the adsorption of benzene vapour on platinum. It is noteworthy that the adsorption is much greater on platinum than on the surface of silica or glass.

It would have been interesting to continue the experiments at temperatures above 32°, but as the apparatus used was limited to measurements of less than 130 mm., determinations of adsorption at higher temperatures and pressures have been postponed. The results in Table III show that from 295°K. to 300°K. the amount of benzene vapour adsorbed on a platinum surface at the saturation

TABLE III.

Benzene–Platinum.

T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.	T K.	p.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.
		No. 1.					No. 7.		
295·4°	83·84	346·0	120·5	0·0	299·2°	100·02	453·4	157·8	0·0
295·6	84·50	275·4	95·9	1·5	299·4	100·78	379·6	132·1	1·6
295·8	84·96	231·7	80·7	3·9	299·6	101·66	285·5	99·4	1·9
296·0	85·60	164·6	57·3	4·8	299·8	102·42	211·6	73·6	2·0
296·5	86·28	104·2	36·2	14·0	300·0	102·98	151·1	52·6	4·2
297·0	86·88	53·74	18·7	23·5	300·5	103·92	60·47	21·0	12·1
298·0	87·47				301·0	104·35	26·87	9·3	23·3
299·0	87·91				302·0	104·90			
301·0	88·75				303·0	105·44			
					304·0	105·86			
		No. 3.					No. 8.		
295·6	84·60	366·0	127·4	0·0	299·9	103·06	456·7	159·0	0·0
295·8	85·20	305·6	106·4	2·3	300·0	103·46	403·7	143·8	1·5
296·0	85·96	225·1	78·3	2·4	300·2	104·24	335·9	116·9	2·7
296·3	86·79	137·7	49·0	4·3	300·5	105·19	241·8	84·1	5·8
296·5	87·23	97·40	33·9	7·6	301·0	106·52	110·9	38·5	11·0
297·0	87·90	36·95	12·8	13·2	302·0	107·62	30·23	10·5	31·8
297·5	88·23	30·23	10·5	28·8	303·0	108·17			
298·0	88·46				304·0	108·60			
301·0	89·46				305·0	109·10			
303·0	90·17								
		No. 5.					No. 9.		
296·4	87·93	382·9	133·3	0·0	301·3	109·95	399·6	139·1	0·0
296·5	88·19	349·3	121·6	1·1	301·5	110·82	315·7	109·9	0·9
296·7	88·79	309·0	107·5	2·8	301·8	111·77	221·6	77·1	3·7
297·0	89·70	201·7	70·1	4·6	302·0	112·37	161·3	56·1	5·8
297·5	90·55	124·3	43·2	12·8	302·5	113·34	77·25	26·8	13·4
298·0	91·25	60·47	21·0	21·8	303·0	113·74	50·38	17·5	25·3
299·0	91·93	20·15	7·0	44·8	304·0	114·42			
300·0	92·35				305·0	114·96			
301·0	92·69				306·0	115·46			
303·0	93·45								
		No. 12.					No. 12.		
304·0	123·85	268·7	93·5	0·0	305·5	126·72	20·16	7·0	35·8
304·1	124·21	235·1	81·8	1·5	306·5	127·30			
304·3	124·85	171·3	59·6	3·2	308·0	127·99			
304·5	125·22	151·1	52·6	7·6	310·0	128·92			
305·0	126·08	68·73	23·3	12·9					

pressure increases with increasing temperature and pressure; and that from 300°K. to 305°K., and perhaps above 305°K., the adsorption falls off rapidly with rising temperature and pressure.

The strikingly large adsorption of benzene on platinum is of great interest, for it is from 5 to 7 times greater than that on glass or silica, and it is slightly greater at certain temperatures than the adsorption of water on silica or platinum.

The Isosteric Heat of Adsorption of Benzene Vapour on Platinum.

The isosteric molar latent heats of adsorption may be calculated from the equation $L = RT^2 d \log p_\theta / dT$ from the measurements of pressure, temperature, and amount adsorbed given in Table III, where L_θ is the isosteric molar latent heat of adsorption at constant pressure, p_θ, and constant amount adsorbed, θ (see Lenher, *loc. cit.*, p. 1790; Coolidge, *J. Amer. Chem. Soc.*, 1926, **48**, 1795). Values of L_θ for several isotherms at different amounts adsorbed are given in Table IV.

TABLE IV.

L_θ (cals. per mol.).

θ.	297° K.	297·5° K.	298·5° K.	299° K.	299·5° K.	300° K.	301° K.	302° K.
20	—	8440	7790	8070	8790	—	—	—
40	8890	9330	—	8050	8040	—	8140	8190
60	9050	—	8430	—	—	8300	—	—
80	8890	—	8280	—	—	8240	—	8200
100	8450	—	8210	—	—	8000	—	8180
120	8640	—	8110	—	—	—	—	—

The latent heat of condensation of benzene at constant pressure from saturated vapour to liquid varies from 8083 cal. per g.-mol. at 296°K. to 7968 cal. per g.-mol. at 304°K. The isosteric heats of adsorption given above are, within the limits of the accuracy of integration, little different from the latent heats of condensation at the same temperatures. This is in agreement with the results of Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146), who measured the "net" heats of adsorption of many organic liquids on charcoal and found that L_θ was of about the same magnitude as the heat of condensation to liquid. Lamb and Coolidge concluded, from considerations of the heats of adsorption, volume relations in the adsorbed films of different substances, and the area of the adsorbing surface, that the vapours were deposited in a liquid film which was usually many molecules thick. The heats of adsorption of benzene given above, together with the measurements of the vapour pressure of benzene approaching the saturation pressure, are strong evidence that the forces or other causes which bring about adsorption act through a thick multimolecular film.

Discussion.

An explanation was previously outlined (Lenher, *loc. cit.*, p. 1788) which accounted for this pre-condensation adsorption at a solid–vapour interface, and traced the probable course of adsorption on a solid surface over a pressure range from high vacuum to saturated vapour pressure. With very low pressures of the vapour over a perfectly clean surface, the first effect will be the building up of a unimolecular layer of the type which Langmuir has studied on metallic and glass surfaces. The range of pressure over which this primary film is built up is probably quite small, as the great attractive forces acting from a bare surface must rapidly hold vapour molecules within their range. Carver (*J. Amer. Chem. Soc.*, 1923, 45, 63) found that at 0° a pressure of 0·2176 mm. of toluene vapour caused only 12% of a glass surface to be covered with toluene molecules; in this case, the unimolecular film is still being built up at 3% of the saturation pressure. When a certain definite value of the equilibrium pressure of the adsorbing substance is reached the unimolecular layer will be compact and complete. With further increase of amount, adsorbed films of varying thickness are deposited, perhaps at first with little, if any, change of pressure. A somewhat similar phenomenon has been observed in measurements made recently in this laboratory on the adsorption of various alcohols from aqueous solutions of very low concentrations on active charcoal (Garner, Faraday Society Discussion, October 1, 1926; Knight, unpublished research). We know in the present case that the formation of the multimolecular liquid film does not begin until more than 95% of the saturation pressure is reached. Trouton (*Rep. Brit. Assoc.*,1907, 453; 1911, 328) has observed these two types of adsorption and he estimates the transition pressure to be about 50% saturation in the case of water vapour being adsorbed on a glass surface.

It is of interest to compare the actual thicknesses of the adsorbed films at corresponding pressures, (p_θ/p_w) (p_w is the saturated vapour pressure), as suggested by Williams, in order to follow the variations in the effective range of the attractive force from the surface. The corresponding pressure $p_\theta/p_w = 1$, or saturation, gives the most instructive results. The thicknesses of the saturated equilibrium films of water and benzene on the three surfaces at the highest and lowest temperatures of investigation are summarised in Table V.

TABLE V.

Water Vapour.		*Benzene Vapour.*	
On glass at 25°	$5{\cdot}3 \times 10^{-5}$ cm.	On glass at 25°	$1{\cdot}1 \times 10^{-6}$ cm.
On platinum at 20·5°	$6{\cdot}4 \times 10^{-7}$,,	On platinum at 22·4°	$7{\cdot}0 \times 10^{-6}$,,
On platinum at 29·5°	$1{\cdot}1 \times 10^{-6}$,,	On platinum at 26·9°	$9{\cdot}3 \times 10^{-6}$,,
On silica at 17·8° ...	$4{\cdot}5 \times 10^{-7}$,,	On platinum at 31°	$5{\cdot}5 \times 10^{-6}$,,
On silica at 28·4° ...	$1{\cdot}4 \times 10^{-6}$,,	On silica at 19°	$1{\cdot}9 \times 10^{-6}$,,
		On silica at 28·7° ...	$1{\cdot}2 \times 10^{-6}$,,

Assuming that all the adsorption measured takes place on a plane surface, we see that at high vapour pressures, in cases where there is no possible chemical attraction of the primary or secondary valence type, films of the order of 50 to 100 molecular layers are deposited. Apparently even when a liquid is present in bulk at a solid–liquid interface the surface forces from the solid exert a force through many layers of the liquid.

The calculation of the amount of benzene adsorbed on a solid surface rests on the assumption that the Boyle–Charles law, $pv = nRT$, applies to benzene vapour close to the saturation point at ordinary temperatures, and it has been suggested that the foregoing conclusions may be vitiated by the slight deviations of this law from absolute accuracy in the particular circumstances. In the present experiments, the temperature range of the measurements may be divided into two parts for consideration: (1) that region in which the pressure of benzene vapour increases linearly with temperature, and in which the validity of the assumption of the Boyle–Charles law can be tested; and (2) the region in which *apparently* the law is not obeyed, and where the observed deviation from the ideal law is attributed to the adsorption or desorption of vapour from the walls of the containing vessel. That the law holds in the region where there is no measurable adsorption of this type (at temperatures more than 1° above the saturation temperature in the case of benzene) is shown by the following consideration: The Boyle–Charles law states that at constant volume and constant amount of vapour p/T should remain constant; this is verified for benzene vapour, because the value of p/T calculated from the experimental data remains constant within $\pm$ 0·0001, the actual values of p/T in different experiments ranging from 0·2600 to 0·4000. A variation of 0·0001 in the value of p/T from that required by the law would make an error of $2{\cdot}34 \times 10^{14}$ in the number of molecules adsorbed per sq. cm. (N/cm.^{2}), and an error of 0·81 in the value of θ, the number of molecular layers adsorbed. As this possible error is of the same order as the accuracy of measurement, the assumption of the ideal-gas law is justified in this calculation.

In the temperature region from saturation to 1° above saturation, the abnormal increase in pressure above that demanded by the ideal-gas law for the increase of pressure with temperature of a vapour at constant volume is attributed directly to the desorption of vapour molecules from the walls of the vessel. There seems to be no other cause to which this unusual pressure increase may be properly ascribed. Benzene vapour is not an associated vapour which would dissociate on heating slightly (in this case, heating 1°) to give the additional number of molecules to exert the measured increase in pressure. A careful consideration of the possible physical causes of this abnormal pressure rise near the saturation temperature indicates that there are no grounds for doubting the application of the Boyle–Charles law to benzene vapour over the region from saturation to the region where it has been shown that this law is obeyed. From the nature of the problem no more direct test of the applicability of the law to this limited region can be made, for all measurements will be vitiated by the adsorption effect observed in this research.

The replacement of the law by a more correct equation of state, *e.g.*, $p(v - b) = nRT$, would not materially affect the conclusions set forth. The equation on which the adsorption calculations are based is $n - n_1 = (p/T - p_1/T_1)v/R$ (see McHaffie and Lenher, *loc. cit.*, p. 1565); using the other equation of state, this becomes $n - n_1 = (p/T - p_1/T_1)(v - b)/R$, where b is the volume occupied by the benzene molecules themselves. For the adsorption vessels used, v varies from 5·317 c.c. to 13·307 c.c.; in the experiments, the values of b vary from $1{\cdot}3 \times 10^{-5}$ to $2{\cdot}7 \times 10^{-5}$ c.c. Thus it is clear that the ratio $v/(v - b)$ may be taken to be equal to unity for the present purpose, and it is obvious that the application of a correction to the Boyle–Charles law is unnecessary in the present case of a vapour near saturation at ordinary temperatures.

Summary.

The adsorption of benzene vapour at pressures above 90% of the saturated equilibrium pressure has been measured on the surfaces of glass, fused quartz, and platinum. An unusually great adsorption on the platinum surface was observed. The free energy changes accompanying the adsorption were calculated.

The isosteric heat of adsorption at constant pressure of benzene vapour on platinum has been calculated from the adsorption isotherms; within the accuracy of calculation, it is found to be of the same magnitude as the latent heat of condensation to liquid.

The adsorption of vapours on solid surfaces over a wide range of pressure is briefly discussed.

A table is given showing the thickness of films exerting the saturated equilibrium pressure.

The author expresses his thanks to Professor F. G. Donnan, F.R.S., for his constant interest and valuable advice during the progress of this research.

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[*Received, November 9th,* 1926.]

XLV.—*The Density of Boron Trichloride and the Suspected Variation in the Atomic Weight of Boron.*

By Henry Vincent Aird Briscoe, Percy Lucock Robinson, and Harold Cecil Smith.

A technique for the determination and comparison of liquid densities with great precision by means of glass floats has recently been developed in this laboratory (Robinson and Smith, J., 1926, 1262) and applied to the problem of the constancy of the atomic weight of silicon derived from different sources. As the differences disclosed in this case did not exceed 0·005 unit, *i.e.*, 1 part in 5612, it seemed advisable to apply this method to boron, where a maximum difference of 0·023 unit, *i.e.*, 1 part in 540, was originally found by measuring the ratio $BCl_3 : 3Ag$ (Briscoe and Robinson, J., 1925, **127**, 696) and subsequently confirmed by a measurement of the density of pure fused boric oxide glass prepared from the same sources (Briscoe, Robinson, and Stephenson, J., 1926, 70).

Outline of the Present Investigation.

In the last stage of the purification, the samples of boron trichloride (Briscoe and Robinson, *loc. cit.*) had been divided by fractional vacuum-distillation into three fractions, and the middle fraction had been used for analysis. In the present investigation, the remaining fractions of each sample were combined and purified by two further distillations in a vacuum, with the rejection of lighter and heavier fractions in each distillation, and the densities of the final main fractions were determined. In the case of two out of the three samples, the liquids forming the final main fractions were distilled fractionally on to and away from the floats, and the densities of the several runnings were thus obtained. From these data, the mean density of boron trichloride, its coefficient of thermal expansion, and the relative atomic weight of the samples of boron present in the various fractions were calculated.

Preparation of Boron Trichloride.

The original sources of the boron used in the three preparations of the trichloride were:

No. 1. Colemanite (calcined) from Death Valley, California, U.S.A.

No. 2. Crude boric acid from the neighbourhood of Volterra, Tuscany.

No. 3. Boracite from Sultan Tchair, Asia Minor.

Each sample, after receiving the uniform and rigorous purification previously described, had been finally divided into five fractions designated T_6, *M*ɪɪɪ, *M*ɪɪ, *M*ɪ, and H_5 (J., 1925, **127**, 704, Fig. 1). T_6 and H_5 were small tail- and head-fractions of about 5—10 c.c., *M*ɪɪ was the main fraction for analysis, and *M*ɪɪɪ and *M*ɪ were tail- and head-fractions similar in size to *M*ɪɪ. *M*ɪɪɪ and *M*ɪ had been preserved in the original containers, having special joints which were now attached to a train (Fig. 1) carrying a head-fraction bulb, H, and a container with a special joint, A. *M*ɪɪɪ and *M*ɪ were arranged so that the plunger tubes, P, were at right angles to one another, thus enabling the capillary of either special joint to be broken by moving the apparatus in the appropriate way. The apparatus was internally cleaned with the usual elaborate precautions, and after assembly was evacuated at X six times, being heated to 150° during each evacuation and thereafter slowly refilled with carefully dried air. Then it was sealed off with the McLeod gauge registering a pressure of 0·01 mm. The special joint of *M*ɪ was then broken and a head-fraction was distilled into H and sealed off. The rest of the contents of *M*ɪ was distilled into A. The special joint of *M*ɪɪɪ was then broken and its contents were distilled into A with the exception of a small tail-fraction; A was then removed by sealing off. This procedure was based on the assumption that, whatever impurity the material might contain, that in *M*ɪ would

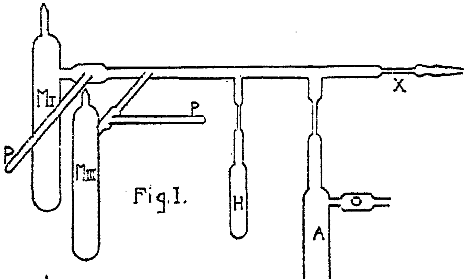

Fig. 1.

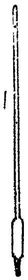

Fig. 3.

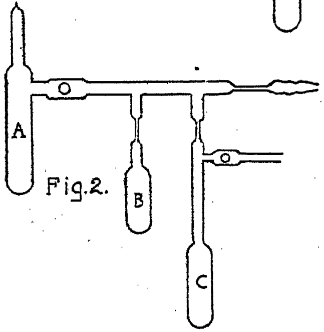

Fig. 2.

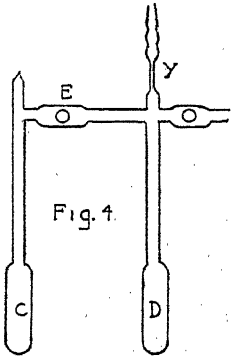

Fig. 4.

probably have a lower b. p. and that in *M*III a higher b. p. than boron trichloride.

The vessel A was now attached to a second train (Fig. 2) which, after cleaning and drying as described above, was sealed off from the pump when the pressure had remained below 0·01 mm. for 30 minutes. B was thoroughly cooled with liquid air, the special joint of A was broken, and the small head-fraction which immediately collected in B was sealed off. C, which contained the two floats, was then cooled with liquid air and the material in A was very slowly and completely distilled at a temperature well below 0°. There were barely visible solid residues left in A from samples No. 2 (Tuscany) and No. 3 (Asia Minor), but there was a small although perceptibly greater residue in No. 1 (California). After the removal of C this residue, which was of the usual gummy character, was warmed and intumesced in the manner previously noted (Briscoe and Robinson, *loc. cit.*).

The Preparation and Standardisation of the Floats.

(The experimental work following is given in outline, and the references, unless otherwise stated, are to Robinson and Smith, J., 1926, 1262, where details may be found.)

The "Durosil" glass floats were prepared precisely as were those used in the determination of the density of silicon tetrachloride; they were rather shorter, as the volumes of the liquids available were less, and the densities of the individual floats of each series were closer together, the maximum difference being in the upper series 0·000194, and in the lower 0·000181.

Previous workers have given for the density of boron trichloride 1·35 at 17·5° (Wohler and Deville, *Compt. rend.*, 1857, **45**, 888) and 1·43386 at 0°/4° (Ghira, *Z. physikal. Chem.*, 1894, **12**, 768; *Gazzetta*, 1893, **23**, i, 452). As these results were too divergent for the present purpose, a preliminary measurement was made. An all-glass hydrometer (Fig. 3) (suitably constructed from a piece of glass tubing of 0·8 cm. bore, with a solid sinker, a body 2 cm. long, and a fine stem 6 cm. long and 0·6 mm. in diameter) was calibrated in a series of bromotoluene–ethyl alcohol mixtures by measuring the length of exposed stem with a cathetometer. The densities of these mixtures were obtained with a Westphal balance. This little hydrometer, which had a range of 1·360—1·417 for a stem exposure of 2·390 cm. and gave readings to about 0·001, is detailed here because of its obvious convenience for such purposes as the present. A number of fractions of boron trichloride from the four-column still (Briscoe and Robinson, *loc. cit.*) were collected into a single vessel, sealed up over mercury for a fortnight, and then distilled in a vacuum on to the hydrometer. A density of 1·350/11° was indicated, which is in reasonable agreement with the value of Wohler and Deville.

An extensive series of liquids and mixtures was reviewed with regard to suitability for float calibration, *n*-propyl bromide (*d* 1·364/18°) being eventually selected. This liquid, from The British Drug Houses, Ltd., had *d* 1·346/19°, as measured by the Westphal balance. Two floats, with flotation-temperatures 10·14° and 15·20°, respectively, in *n*-propyl bromide, were tried out in the boron trichloride previously used for the hydrometer test by transferring the liquid *via* a special joint to another vessel containing the floats. The flotation-temperatures in boron trichloride were 7·45° and 11·19°, respectively; and it was therefore decided to work to flotation-temperatures of 10° and 12°, respectively (*i.e.*, below the b. p. at atmospheric pressure), these being equivalent, respectively, to 14° and 16° in *n*-propyl bromide. It was early noticed that the density of this liquid decreased with time (compare bromobenzene, *loc. cit.*), and the specimen used in the final calibration was therefore purified by one rough, followed by two careful, distillations with the rejection of head- and tail-fractions, the boiling points, taken every minute, having mean values 71·40°/756·8 mm. and 71·75°/760·2 mm. The standardisation of the floats was repeated with the once-, twice-, and thrice-distilled *n*-propyl bromide in the same apparatus (except that the float-lifter was of platinum, as nichrome was attacked), and with all the precautions previously described (*loc. cit.*), 161 flotation-temperatures being taken. As even the purified liquid tended to decrease in density with time, the final measurements for the six floats were completed within 8·5 hours of the third distillation, the flotation-vessel being then corked up. On the following day, the density of the liquid was determined at 16·857° and 20·873°, with the pyknometers and by the method previously described (*loc. cit.*), the results being 1·351288 and 1·344572, respectively. Immediately afterwards two check flotation-temperatures were taken, the same liquid being used to establish the constancy of its density. These results are given in Table I which illustrates both the change in density of the *n*-propyl bromide and the increased permanency of its density with purification.

The Density of the Three Samples of Boron Trichloride at 11°.

Flotation-temperatures were obtained in exactly the manner described for silicon tetrachloride, except that, as the temperatures were constantly below that of the room, the bath was maintained in the required condition by a variable stream of ice-cold water from another tank. This arrangement was found to give excellent

TABLE I.

The Standardisation of the Floats in *n*-Propyl Bromide.

Float.	Flot.-temp. (C_3H_7Br once distilled).	Flot.-temp. (C_3H_7Br twice distilled).	Flot.-temp. (C_3H_7Br thrice distilled).	Density (g./c.c.).	Flot.-temp. (check after density detern.).
U	13·884°	16·922°	17·229°	1·350666	17·223°
Y	13·794	16·838	17·134	1·350825	
Z	13·819	16·819	17·121	1·350847	
V	15·809	18·909	19·223	1·347331	
W	15·839	18·787	19·106	1·347525	
X	15·849	18·802	19·123	1·347499	19·111

temperature regulation. About 130 flotation-temperatures were observed and those actually used differed by less than 0·010° for rising and falling temperatures. The floats showed markedly less tendency to become electrically charged than was the case in silicon tetrachloride (*loc. cit.*); the charges were most in evidence in the Asiatic sample, but even these were sufficiently reduced after two hours to allow flotation-temperatures to be taken. The charges were again positive in character (*loc. cit.*). Table II gives these results with the corresponding densities, the value 15×10^{-6} being used as the coefficient of cubical expansion of "Durosil" glass (Robinson and Smith, J., 1926, 3152). Table III gives the coefficients of cubical expansion calculated from the same data, together with the calculated probable error of the mean.

TABLE II.

The Density of Boron Trichloride.

Source.	Float.	F.-t. in BCl_3.	*D* at f.-t.	*D* of BCl_3 at 11·000°.	Diff. from mean.
California	Y	10·351°	1·350963	1·349478	+0·000157
	X	11·800	1·347647		
Tuscany	U	10·326	1·350805	1·349273	−0·000048
	V	11·788	1·347482		
Asia Minor	Z	10·229	1·350987	1·349213	−0·000108
	W	11·666	1·347676		
			Mean	1·349321	±0·000104

TABLE III.

The Coefficient of Thermal Expansion of Boron Trichloride.

Source.	Coeff. of exp.	Diff. from mean.
California	0·0016981	+0·0000004
Tuscany	0·0016868	−0·0000109
Asia Minor	0·0017073	+0·0000096
Mean	0·0016977	±0·0000070

Calculated probable error on mean, 0·0000040.

In Table IV are given the relative atomic weights of the boron present in the three samples, calculated by making the usual assumptions (*loc. cit.*) and taking Asiatic boron trichloride, *d* 1·349213 and atomic weight 10·818, as standard (the same standard is used throughout this paper). Table IV also includes for the sake of comparison the previous results of Briscoe and Robinson (*loc. cit.*) and of Briscoe, Robinson, and Stephenson (*loc. cit.*).

TABLE IV.

Source.	*D*.	At. wt. from *D*.	At. wt. from $BCl_3 : 3Ag$.	At. wt. from *D* of B_2O_3.
California	1·349478	10·841	10·841	10·847
Tuscany	1·349273	10·823	10·823	10·825
Asia Minor	1·349213	10·818	10·818	10·818

For reasons dealt with more particularly below, the Californian and the Asiatic material underwent the further investigation next described. The flotation-vessels were severally attached to second containers constructed with long stems and special joints as illustrated (Fig. 4), to enable both vessels to be submerged to the same level in the bath. These were cleaned and dried with the usual precautions, being evacuated and refilled with dry air six times, with heating each time to about 150°, and were finally sealed off at Y when a pressure of 0·007 mm. had been registered for 30 minutes. After final check flotation-temperatures had been taken, the liquid in C was cooled with solid carbon dioxide and the special joint, E, was broken. This arrangement enabled the following operations to be performed: (*a*) distillation from C to D with determination of densities at intervals so long as there remained sufficient liquid to allow of the movement of one float; (*b*) pouring from C to D and distillation from D to C with density determinations at intervals as soon as there was sufficient liquid in C; (*c*) washing, by distilling a little liquid from the main bulk into the other vessel and then pouring back. Actually the material in C was distilled into D in stages, solid carbon dioxide being used as the cooling agent and bumping avoided by slightly cooling C; densities were taken at intervals. The residual liquid was then poured into D, and on three occasions small quantities were distilled into C and poured back into D. From D, which now held the whole of the liquid, it was distilled in stages on to the clean floats in C, densities being taken at intervals as soon as possible. These two sets of measurements were then repeated as a check. The numerous observations of flotation-temperatures in which two floats were used soon demonstrated that the temperature interval between the two floats was sufficiently constant to permit the use of one float only when this was convenient. Tables V and VI give the data for the Californian and the Asiatic boron trichloride, respectively.

TABLE V.

Californian Boron Trichloride.

1. Distilling from C to D.

	Flotation-temperatures.			
Amount on floats.	Float Y.	Float X.	Observed temp.-interval.	Density.
Total.	10·351°	11·800°	1·449°	1·349478
11/12 tail.	10·366	11·816	1·450	1·349514
10/12 „	10·381	11·829	1·448	1·349545
9/12 „	10·392	11·844	1·452	1·349575
8/12 „	10·406	11·854	1·448	1·349602
7/12 „		11·871		1·349639
		Mean	1·449	

2. Distilling from D to C.

Amount on floats.	Float Y.	Float X.	Observed temp.-interval.	Density.
6/12 head.		11·738		1·349337
7/12 „		11·738		1·349337
8/12 „		11·741		1·349344
9/12 „		11·741		1·349344
10/12 „		11·744		1·349351
11/12 „		11·756		1·349378
Total (distilled).		11·796		1·349469
Total (washed).*	10·350	11·800	1·450	1·349478

TABLE VI.

Asiatic Boron Trichloride.

1. Distilling from C to D.

	Flotation-temperatures.			
Amount on floats.	Float Z.	Float W.	Observed temp.-interval.	Density.
Total.		11·670°		1·349212
13/15 tail.		11·683		1·349241
11/15 „		11·688		1·349252
9/15 „		11·699		1·349279
7/15 „	10·256°	11·701	1·445°	1·349281
5/15 „	10·259	11·707	1·448	1·349293

2. Distilling from D to C.

Amount on floats.	Float Z.	Float W.	Observed temp.-interval.	Density.
7/17 head.	10·226	11·666	1·440	1·349213
10/17 „		11·673		1·349219
12/17 „	10·222	11·662	1·440	1·349207
14/17 „		11·670		1·349212
16/17 „	10·223	11·668	1·445	1·349213
Total (distilled).		11·679		1·349234
Total (washed).*		11·680		1·349235
		Mean	1·444	

* "Washed" indicates that a small amount of liquid had been poured back on to the residue and then poured forward again, and this operation repeated three times.

Discussion of Results.

The Density.—The relative error of the densities given above is probably less than ± 0·000002, whilst the absolute value may, for reasons given elsewhere (*loc. cit.*), be as much as ± 0·00005 from the truth. The authors conclude that the values for the Californian, Tuscan, and Asiatic materials are 1·349353, 1·349273, and 1·349211, respectively, giving a mean density of 1·349279 at 11·000° ± 0·005° for an average sample of boron trichloride, these results being absolute and independent of the expansion of glass.

The Coefficients of Expansion.—The values given in Table VII for Californian and Asiatic materials are both derived from the mean of six intervals of temperature, whilst that for Tuscany boron is taken from Table III. The coefficients of expansion at 10° have a mean value of 0·0016954 with an error probably less than ±0·000005, and a calculated probable error of ± 0·0000030. These results are absolute. Apparently this physical constant for boron trichloride has not been determined previously.

TABLE VII.

Source.	Mean temp.-interval.	Coeff. of exp.	Diff. from mean.
California	1·449	0·0016981	+0·0000027
Tuscany	1·462	0·0016868	−0·0000086
Asia Minor	1·444	0·0017014	+0·0000060
	Mean	0·0016954	±0·0000058

Calculated probable error, 0·0000030.

The Relative Atomic Weights.—The relative atomic weights derived from a comparison of the density of the whole bulk of material from the three sources (see Table III) are in remarkable agreement with those of Briscoe and Robinson (*loc. cit.*), but as they were combinations of a head- and a tail-fraction taken before and after the portion analysed, with comparatively little subsequent rejection, it was clearly desirable to ascertain whether they were of uniform composition. Previous work upon the $BCl_3 : 3Ag$ ratio had indicated that a higher apparent atomic weight was to be expected in both the head- and the tail-fractions. The higher value for the latter was easily explained by assuming the presence of boric oxide or silicon tetrachloride, whereas the higher value for the head fraction, although it had been independently observed by Baxter and Scott (*Proc. Amer. Acad. Arts Sci.*, 1923, **59**, 21), was difficult to account for, because the impurities to be anticipated here, *e.g.*, hydrogen chloride and chlorine, are such as would give a lower apparent atomic weight. From the data in Tables V and VI the density and corresponding apparent atomic weight of the separate fractions have been calculated and are given in Table VIII.

It is evident that in each case the extreme heads show a markedly lower density, and it may be presumed that this is related to the unexplained higher apparent atomic weight in the fractions mentioned above. On the other hand, the higher density in the case of the tail-fractions is very obvious, particularly in those of the Californian sample, where, as its effect is somewhat spread, *i.e.*, over the

TABLE VIII.

Source : California.			Source : Asia Minor.		
Head-fractn. Twelfth.	Density.	At. wt.	Head-fractn. Two-fifteenths.	Density.	At. wt.
1st	1·349082	10·807	1st	1·349024	10·802
2nd	1·349204	10·817	2nd	1·349181	10·815
3rd	1·349285	10·824	3rd	1·349131	10·811
4th	1·349359	10·831	4th	1·349272	10·823
5th	1·349343	10·829	5th	1·349251	10·821
6th			Seventeenth.		
7th	1·349337	10·829	8th, 9th, and 10th	1·349233	10·819
8th	1·349393	10·833	11th and 12th	1·349147	10·812
9th	1·349344	10·829	13th and 14th	1·349242	10·820
10th	1·349414	10·836	15th and 16th	1·349220	10·818
11th	1·349648	10·856	17th	1·349570	10·849
12th	1·350470	10·927			

10th, 11th, and 12th twelfths, it may be due to the presence of silicon tetrachloride as well as boric oxide. With the Asiatic material the effect is only noticeable in the last seventeenth and is probably accounted for entirely by the presence of boric oxide. Undoubtedly the liquid of Asiatic origin is the purer of the two samples in respect of less volatile materials, and this makes it difficult to select the figures which should be employed to arrive at the respective means. This difficulty has been avoided by arbitrarily taking means of (i) the first half, (ii) the first three-quarters, (iii) the middle half: these results are tabulated in Table IX.

TABLE IX.

	Californian.	Asiatic.	Difference.
(i)	10·823	10·813	0·010
(ii)	10·825	10·814	0·011
(iii)	10·830	10·817	0·013

These figures suggest that there is a real difference between the atomic weights of the two samples of boron, although this difference would seem to be less than that previously indicated by the BCl_3 : 3Ag ratio. This discrepancy is explained by the traces of impurity disclosed in the Californian material in the course of the present investigation.

The authors desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of them (H.C.S.) to take part in this inquiry, and to express their thanks to Captain F. P. Mills of the Northumberland and Durham Rescue Brigade for kindly supplying the necessary liquid air.

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[*Received, November 13th, 1926.*]

XLVI.—*The Ignition of Gases. Part VI. Ignition by Flames. Mixtures of the Paraffins with Air.*

By NOEL STANLEY WALLS and RICHARD VERNON WHEELER.

ONE of the objects of the research of which the present paper forms a part has been to determine, more particularly in relation to problems of safety in coal mines, which mixtures of methane (firedamp) and air can be most readily ignited. It has been shown that this question can only be answered fully when the means of ignition are specified, for the answer depends primarily on the nature of the source of ignition.

For example, mixtures containing 5—6% of methane have been found to be the most readily ignited by the walls of a heated chamber into which they are admitted, the temperature required being lowest for these mixtures (J., 1922, **121**, 2079); but when the source of ignition is an electric spark, whether capacity or inductance, mixtures containing 8·25—8·5% are the most readily ignited, the sparks just capable of igniting them having the least energy (J., 1920, **117**, 903; 1925, **127**, 14).

The essential difference between these two sources of ignition lies in their time of contact with the mixture to be ignited, with respect to which they represent extremes, the heated surface being a maintained, and the electric spark a momentary, source of heat. It has been shown that ignition by a heated surface is not instantaneous; at the "ignition-temperature," * the time of contact between the heated surface and the mixture required before inflammation can occur may be many seconds, whilst even at temperatures several hundred degrees higher than the ignition temperature there is a measurable lag on ignition. On the other hand, we have given reasons for believing that the study of the ignition of gases by a momentary source of heat of high temperature should be regarded more as a study of the propagation of flame than of its initiation (J., 1924, **125**, 1858), flame spreading away from the path of an electric discharge most readily in those mixtures in which the speed of propagation normally is fastest.

It will be realised that a heated surface, even at a very high temperature, would fail to ignite a gaseous mixture if it did not remain in contact with it beyond the duration of the period of "lag," and it can be understood that any source of ignition of high intensity, *e.g.*, a flame, might fail for the same reason. Flames can, indeed, be projected into explosive mixtures of methane and air without igniting them, a fact which suggested means of determining the relative ignitability of different mixtures of methane and air, for, although any sustained flame is at a temperature sufficiently high to ignite any mixture of methane and air,* it should be possible, by limiting the time of exposure of a flame of given character to different mixtures, to discriminate between them.

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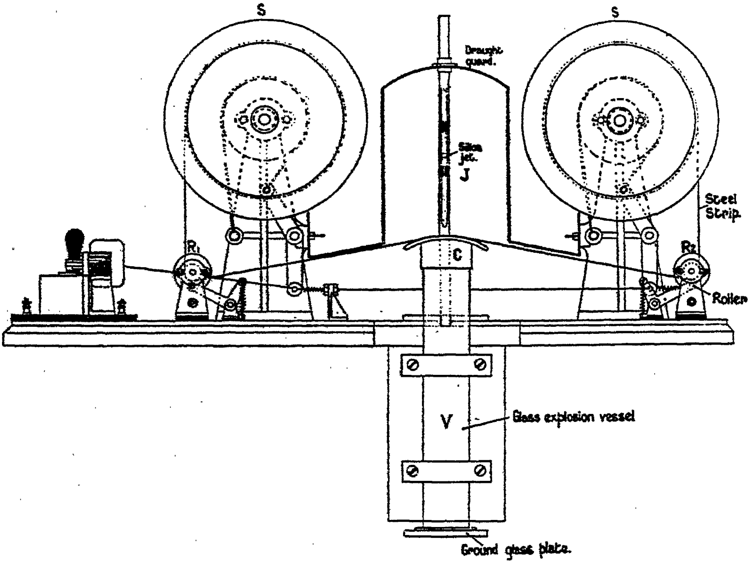
* *I.e.*, the lowest temperature, under the conditions of experiment, at which inflammation takes place, no matter how long the surface remains in contact with the mixture.

Preliminary experiments (Safety in Mines Research Board, Paper No. 24, 1926) showed that the lag on ignition of mixtures of methane and air by flames was sufficiently long to permit of accurate measurement, and that the duration of the lag varied with the composition of the mixture. An apparatus was therefore devised to measure the minimum time of exposure necessary for a flame of standard character to ignite mixtures of known composition. In this way, the relative ignitabilities of different mixtures could be expressed in terms of the duration of the lag on ignition under the conditions of experiment. The apparatus (for details, see "Experimental") consisted of a glass explosion vessel, V (Fig. 1), with a cap of brass, C, over which a thin steel strip could

FIG. 1.



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* A possible exception is the "cool flame" observed in special circumstances, as in a gently-warmed mixture of ether vapour and air.

be rapidly moved. The exposure of the inflammable mixture to a flame playing vertically downwards from a silica jet, J, was effected when a hole, 1 cm. in diameter, in the steel strip coincided with a hole of the same diameter in the brass cap. The duration of exposure was varied by varying the speed of movement of the steel strip.

It was early found that the flame to be used as the source of ignition of a mixture of given composition must be fully aërated, otherwise it would abstract oxygen from the mixture and alter its composition before igniting it. In a series of experiments, *e.g.*, with methane and air, a false idea would thus be given regarding the composition of the most readily ignitable mixture. The flame used for the experiments described in this paper was a fully aërated coal-gas flame.

A close study of the manner in which the flame was exposed to the mixture during these experiments showed that, although its length when burning in still air was sufficient, its tip did not enter the explosion vessel when the hole in the cap was uncovered by the hole in the steel strip. The disturbance of the air caused by the rapidly moving strip caused the tip of the gas-jet to flatten in such a manner that a disc of flame was presented to the mixture. By adjusting the length of the flame when burning in still air, the diameter of the disc of flame exposed to the mixture during an experiment could be varied. With a flame adjusted to be 1 cm. in length, the disc was about half the diameter of the hole in the brass cap of the explosion-vessel; whilst when the jet was 1·5 cm. long the disc spread completely over the area of the hole. Under the latter conditions, it was not easy, with the apparatus as designed, to discriminate between the durations of exposure required to ignite mixtures of methane and air containing between 8 and 12% of methane, but with the smaller disc of flame marked differences could be measured throughout the range of inflammable mixtures.

Experiments were made with methane, ethane, propane, and pentane in admixture, severally, with air.

Mixtures of Methane and Air.—The results obtained for the lag on ignition of mixtures of methane and air, using three different sizes of disc of flame as the source of ignition, are in Table I. The recorded areas of the discs of flame are approximate. The measurements actually made to ensure that the area of flame was constant in each series of experiments were of the lengths of the jets when burning in still air.

The general conclusion to be drawn from these results is that the mixtures of methane and air most readily ignited by fully

TABLE I.

The Ignition of Methane–Air Mixtures by Flames.

Flame area: 20 sq. mm.		Flame area: 45 sq. mm.		Flame area: 75 sq. mm.	
Methane, %.	Duration of exposure required for ignition (millisecs.).	Methane, %.	Duration of exposure required for ignition (millisecs.).	Methane, %.	Duration of exposure required for ignition (millisecs.).
7·90	12·40	7·95	6·94	7·40	7·50
8·05	9·25	8·15	5·42	8·10	3·64
8·20	8·75	8·20	5·12	8·45	3·62
8·65	7·90	9·35	4·38	9·15	3·61
8·70	7·81	10·80	4·50	9·95	3·53
9·05	7·37	12·70	7·50	10·70	3·56
9·65	6·90			11·10	3·62
10·30	6·90			12·05	3·60
10·85	7·12			12·15	3·63
				12·70	6·69

aërated flames, inasmuch as the time of contact required is shortest, contain 9·5—10·0% of methane.*

The duration of exposure required for ignition to occur, as might be expected, is less the larger the area of the flame used as the source of ignition; whilst, under the conditions of these experiments, the larger the area of the igniting flame the less marked is the differentiation between one mixture and another.

Mixtures of the Higher Paraffins and Air.—There was considerable difficulty throughout this research in maintaining such constancy of experimental conditions as would ensure that the results recorded were strictly comparable one with another, and frequent check experiments with a given mixture, adopted as standard, were necessary. In particular, great care had to be taken to avoid disturbing the position of the silica nozzle at which the igniting flame was produced, for the character of the flame as presented to the mixture to be ignited was thereby altered. If this occurred during a series of experiments, it usually saved time to start the series afresh rather than to attempt to reproduce previous conditions.

The results recorded in Table I for mixtures of methane and air were all obtained under strictly comparable conditions of experiment, but when attempting to continue the series to include the ignition of other paraffins we were not so fortunate. We have determined, however, in individual series not comparable one with another, the most readily ignitable mixtures of ethane, propane, and pentane, respectively, with air. We have also obtained relative values, under standard conditions, for the duration of exposure to a fully aërated flame required for the ignition of each of these most readily ignitable mixtures. From these data, curves can be constructed relating percentages of each combustible gas in air with the time of exposure to a standard flame required to ignite them, and each curve can be assigned its proper position relative to the others. Such curves are reproduced in Fig. 2.

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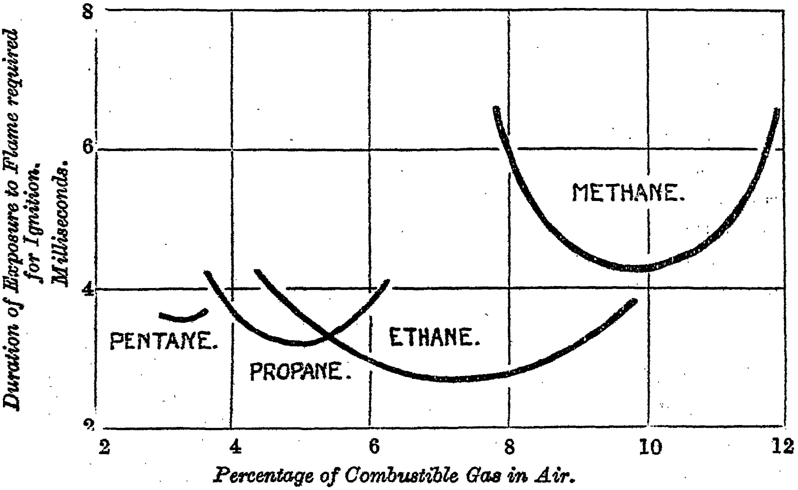
* In earlier experiments, when an under-aërated flame was used, the mixtures containing the lower percentages of methane appeared to be more readily ignitable, for the reason already given. A similar effect has been observed during experiments on the ignition of mixtures of methane and air by heated wires when the wire has been of a readily oxidisable metal.

FIG. 2.



The composition of the most readily ignitable mixture in each instance corresponds fairly closely with that of the mixture in which the initial speed of propagation of flame is most rapid. The values are recorded in Table II.

TABLE II.

Combustible gas.	Mixture in which speed of uniform movement of flame is fastest. (Combustible gas, %.)	Relative speed of flame (cm./sec.).*	Mixture most readily ignited by flame. (Combustible gas, %.)	Relative duration of exposure of flame required (millisecs.).
Methane	9·65	91	9·8—10·0	4·3
Ethane	6·05	127	6·8— 7·0	2·7
Propane	4·45	114	4·8— 5·0	3·2
n-Pentane	2·90	115	3·1— 3·3	3·5

* In a horizontal brass tube 5 cm. in diameter (Mason, J., 1923, **123**, 210).

The deduction to be drawn from these results is that the ease of ignition of an explosive mixture by a momentary source of heat is dependent essentially on the normal speed of propagation of flame in the mixture. Ease of "ignition," therefore, here corresponds with the ability of the flame to travel through the mixture after the source of ignition has been removed. This is the same deduction as was drawn with respect to ignition by the impulsive electrical discharge, and a similar explanation, *viz.*, that a certain minimum volume of an explosive mixture must be burnt in order that there shall be a spreading inflammation through it, can be advanced.

There is thus a marked resemblance between the phenomena of ignition of the paraffin hydrocarbons by means of momentary flames and by means of electric sparks. The resemblance persists when the effect of increasing the area of flame momentarily exposed to the mixtures (see Table I) is compared with the behaviour of capacity and inductance sparks, respectively. Just as increasing the area of the flame renders it more difficult to differentiate between one mixture and another with respect to its ignitability, so does the larger volume of inductance sparks, as compared with capacity sparks, have the effect of masking small differences in the ignitability of those mixtures that are most readily ignited.

EXPERIMENTAL.

Details of the apparatus used for bringing the various mixtures into contact with a flame during a measured small interval of time are as follows.

The steel strip (Fig. 1) was 0·05 mm. in thickness and 3·81 cm. broad. It was wound by means of an electric motor from one spool, S, to another under rollers, R_1 and R_2, between which the explosion vessel was mounted. Arrangements were made whereby the speed of movement of the strip could be accurately measured and, to avoid accidents due to overwinding, its movement automatically stopped a short time after the exposure of the mixture in the explosion-vessel to the jet of flame.

The explosion-vessel was 5·5 cm. in diameter and 50 cm. long. Its upper end was closed by the brass cap, C, as already explained, and the lower end could be closed by a ground-glass cover-plate whilst the mixture to be tested was being introduced. This was done by exhaustion of the air through a tap at the side and its replacement by a mixture of known composition previously prepared in a gas-holder. The hole in the brass cap, which was 1·5 mm. thick, had its lower edge brought to a thin bevel.

In carrying out an experiment, the speed of movement of the steel strip, from which the time of exposure of the flame to the mixture could be calculated, was adjusted roughly so that ignition of the mixture did not occur, and then a series of trials was made with carefully regulated speeds so as to determine accurately the duration of exposure necessary for ignition. The measurements of duration of exposure had a maximum error of 0·012 millisec.

This work has been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish.

THE UNIVERSITY, SHEFFIELD. [*Received, August 31st, 1926.*]

XLVII.—*The Combustion of Complex Gaseous Mixtures. Part III. The Inflammation of Mixtures of Carbon Monoxide and Hydrogen with Air in a Closed Vessel.*

By GEORGE BARTON MAXWELL, WILLIAM PAYMAN, and
RICHARD VERNON WHEELER.

IN Part II of this research (J., 1923, **123**, 1251) reference was made to preliminary experiments on the inflammation of mixtures of carbon monoxide and hydrogen with air, ignited at the centre of a spherical vessel, and some of the results were quoted to show that the "law of speeds" * would apply to the spread of flame in complex gaseous mixtures ignited under such conditions. In the present paper further series of experiments of a like nature are described.

Few measurements by earlier investigators are available of the magnitude and rate of development of pressure when mixtures of carbon monoxide or hydrogen with air are inflamed in closed vessels. Langen's experiments with these gases ("Mitteilungen über Forschungsarbeiten aus dem Gebiete des Ingenieurwesens," 8, 1903) were chiefly with mixtures with pure oxygen, and he was only concerned with measuring the maximum pressures. The rate of development of pressure, under the same conditions of experiment, was examined by Nägel (*ibid.*, **54**, 1908) for hydrogen, but he chose only mixtures containing excess of oxygen. Both Langen and Nägel used a spherical vessel of 34 litres capacity, and ignited their mixtures by an electric spark passed at the centre.

Bone and Haward (*Proc. Roy. Soc.*, 1922, **100**, 67) and Bone,

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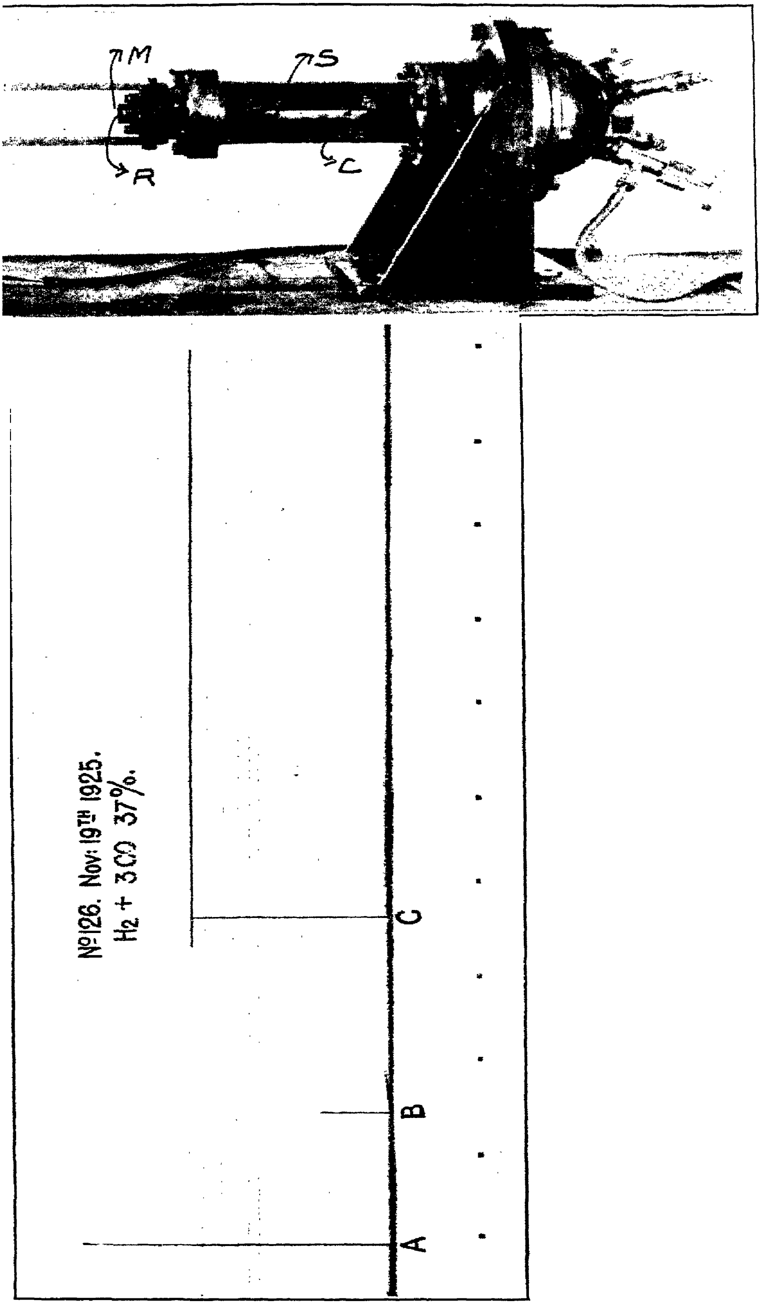
* "Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures, of the same type, propagate flame at the same speed, under the same conditions of experiment" (J., 1922, **121**, 365).

Newitt, and Townend (J., 1923, **123**, 2008) have made measurements of the pressures produced and their rate of development with hydrogen–air and carbon monoxide–air mixtures at various initial pressures up to 50 atm. Their explosion-vessel was spherical, and their source of ignition, a heated platinum wire, was near the wall. Under these conditions, part of the flame is in contact with the wall of the vessel whilst the remainder is travelling through the mixture, so that heat is lost by conduction before the maximum pressure is attained; on the other hand, with central ignition, except when the speed of the flame is very slow, the flame does not reach the boundary of the vessel until the whole of the mixture has been inflamed, *i.e.*, until the instant of maximum pressure.

Crowe and Newey (*Phil. Mag.*, 1925, **49**, 1112) have carried out experiments with mixtures of carbon monoxide and air ignited centrally in a sphere of 40·6 cm. diameter. They have, however, disregarded the effect of water vapour on the rate of combustion of carbon monoxide, and their results are consequently difficult to interpret. Fenning (*Phil. Trans.*, 1926, *A*, **225**, 331) ignited mixtures of carbon monoxide and air, hydrogen and air, and blends of the two mixtures, at the centre of a cylindrical explosion-vessel, 20 cm. long and 18 cm. in diameter, at an initial pressure of 5·2 atm. and an initial temperature of 50°. He also studied the effect of water vapour on the rate of explosion of carbon monoxide.

For the experiments now described, new apparatus was constructed, the general arrangement of which is shown in Fig. 1. The principal new feature was a manometer of the Petavel type, designed to obtain as accurate a measure as possible of the rate of development of pressure with explosions that varied considerably in this respect. The gauge consisted essentially of a steel piston 5 cm. in diameter, screwed into the free end of a tubular steel spring, S. The other end of the spring was attached rigidly to a brass casing, C, which screwed on to the explosion-vessel. When assembled, the face of the manometer piston was flush with the inner wall of the explosion-vessel. Any movement of the piston caused a compression of the spring, which was transmitted, by a steel connecting-rod, R, to a small concave mirror, M, of stainless steel. One end of the connecting-rod was screwed into the piston, whilst the mirror rested in a slot in the other end and was held in position by taut stays of piano-wire, W. Considerable difficulty had been experienced with a previous example of this type of manometer, used in our preliminary experiments, in arranging that it should be equally sensitive in registering explosions of very slow and very rapid development. In the present example, the clearance between the piston and a brass bush which is screwed

FIG. 1.



into the wall of the bomb was exceedingly small, and, unless the piston was frequently removed and carefully cleaned, there was a danger that a film of moisture would form on its periphery. This would cause a frictional force resisting the free movement of the piston. Strict attention has been paid to this point throughout our experiments.

The explosion-vessel was a spherical bomb of 4 litres capacity, fitted with a valve and firing electrodes, similar to that used in earlier work (J., 1918, **113**, 854). A rubber washer between the spring of the manometer and a seating in the wall of the bomb made a gas-tight joint.

A rise in pressure within the explosion-vessel of 1 atm. caused a movement of the piston of 0·0012 mm. This movement was magnified by an optical lever. A beam of light, reflected from the mirror, was focussed on the surface of a strip of sensitised paper carried by a revolving drum. The source of illumination of the mirror was a carbon arc-lamp. The moment of ignition of the mixture was recorded on the sensitised paper by focussing on it, through a telescope, the spark from a gap in series with the spark-gap at the centre of the explosion-vessel. This latter was between pointed electrodes of copper, 3 mm. apart. The spark used to cause ignition was, throughout the experiments, the secondary discharge from a 6-inch induction-coil, using a current of 10 amps. through the primary circuit, the trembler being locked. The rate of revolution of the camera drum was recorded by photographing on it the sparks produced at the mercury contact of an electrically driven tuning-fork, of 100 frequency. A typical record (reduced in size to nearly one-half for reproduction) is shown in Fig. 2. On this record, A is the time of ignition; B, the time of first appearance of pressure; and C, the time of attainment of maximum pressure. The record of the tuning-fork, marking 1/100ths of a second, appears at the bottom of the chart. The speed of revolution of the recording drum was varied according to the rapidity of the explosion. With the most rapid explosions, those of mixtures of hydrogen and air, it was such that a time-interval of 0·01 sec. measured 4·5 cm. on the chart.

Each gas mixture was prepared in a 20-litre glass gas-holder and analysed before use. In each experiment, the bomb was exhausted of air to within a few mm. of mercury, filled with the mixture to be experimented with, re-exhausted, and refilled. The results, both for maximum pressures attained and for rates of development of these pressures, have been checked by explosions of similar mixtures in a bomb of the same dimensions fitted with a different type of manometer. Details of these check experiments, together with the records of pressures, will be given in a later communication. The present paper deals only with the rate of development of pressure.

The main object of the present series of experiments has been to test the application of the law of speeds to the rate of development of pressure when complex gaseous mixtures are ignited in a closed vessel. With this object in view, a series of mixtures has been used of air with hydrogen and carbon monoxide, both individually and also jointly in the proportions corresponding to $3H_2 + CO$, $H_2 + CO$, and $H_2 + 3CO$. Since these experiments also throw light on the effect of water vapour on the combustion of carbon monoxide, a further series of experiments has been made with mixtures of carbon monoxide and air saturated with water vapour at different temperatures. Unless otherwise stated, the mixtures were initially at atmospheric pressure.

Rate of Development of Pressure.

The values obtained for the rate of development of pressure on explosion of the various mixtures, all saturated with water vapour at 15°, are given in Table I, in which the percentage given in col. 1 relates to the inflammable gas shown at the head of each sub-section.

TABLE I.

The Rate of Development of Pressure. Hydrogen, Carbon Monoxide, and Mixtures of the Two with Air. (Saturated with water vapour at 15° and atmospheric pressure.)

Inflammable gas, %.	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure *t* (sec.).	1/*t*.	Mean speed of flame (cm./sec.).
		(*a*) Hydrogen.		
10·2	0·070	0·166	6·0	58
15·1	0·019	0·038	26·3	260
19·4	0·009	0·019	52·6	510
24·5	0·005	0·011	90·9	880
28·9	0·003	0·008	125	1220
34·1	0·003	0·007	143	1390
37·2	0·003	0·007	143	1390
39·3	0·003	0·007	143	1390
44·4	0·003	0·008	125	1220
45·8	0·004	0·008	125	1220
49·0	0·005	0·010	100	970
54·0	0·005	0·011	90·9	880
56·2	0·006	0·013	76·9	750
57·2	0·006	0·015	66·9	650
62·3	0·009	0·020	50·0	440
66·1	0·018	0·033	30·3	290

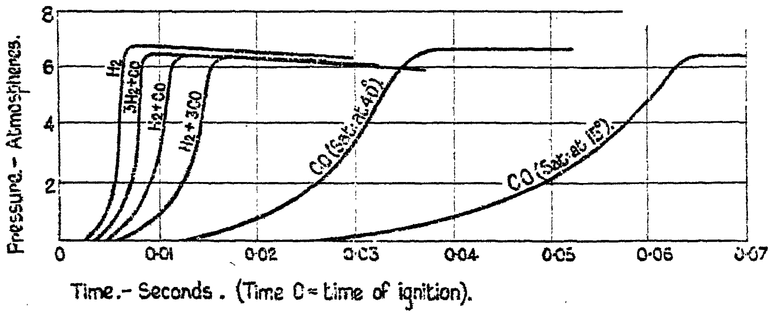
TABLE I (*continued*).

Inflammable gas, %.	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure t (sec.).	$1/t$.	Mean speed of flame (cm./sec.).
(*b*) $3H_2 + CO$.				
14·4	0·036	0·072	13·9	130
20·0	0·012	0·026	38·5	370
24·0	0·007	0·016	62·5	610
29·2	0·006	0·011	90·9	880
37·7	0·004	0·009	111	1080
43·7	0·004	0·009	111	1080
51·0	0·006	0·013	76·9	750
56·5	0·007	0·016	62·5	610
64·6	0·020	0·041	24·4	240
(*c*) $H_2 + CO$.				
15·8	0·037	0·095	10·5	100
18·0	0·024	0·078	12·8	120
24·0	0·009	0·026	38·5	370
28·9	0·006	0·017	58·8	570
33·3	0·005	0·013	76·9	750
38·9	0·005	0·012	83·3	810
43·4	0·004	0·012	83·3	810
56·1	0·006	0·017	58·8	570
60·8	0·017	0·030	33·3	320
(*d*) $H_2 + 3CO$.				
15·9	0·056	0·017	5·9	58
21·0	0·023	0·062	16·1	160
26·8	0·012	0·032	31·1	300
30·0	0·009	0·025	40·9	390
37·0	0·007	0·018	55·6	540
39·3	0·007	0·017	58·8	570
46·3	0·007	0·017	58·8	570
49·1	0·007	0·018	55·6	540
57·6	0·012	0·029	34·5	340
60·7	0·019	0·045	22·2	220
(*e*) Carbon Monoxide.				
21·6	0·050	0·159	6·3	60
23·5	0·050	0·144	16·9	65
28·0	0·029	0·087	11·5	110
31·1	0·026	0·067	14·9	145
36·6	0·027	0·065	15·4	150
39·4	0·027	0·071	14·2	135
44·9	0·025	0·065	15·4	150
49·6	0·023	0·065	15·4	150
54·7	0·032	0·078	12·8	125

Time–pressure curves, reproduced from the records, for each of the maximum-speed mixtures [*i.e.*, those mixtures of inflammable gas and air (or oxygen) in which the proportions of inflammable gas are such that the speed of flame in the mixture, under given experimental conditions, is the fastest obtainable] are shown in Fig. 3 plotted on the same time-scale to enable direct comparison to be made. The curves form a continuous series, of the same general character, from the slow carbon monoxide–air explosion to the comparatively rapid hydrogen–air explosion.

Strictly speaking, the measure of the "rate of development of pressure" should be the increment of pressure per unit of time. Since, however, this is continuously changing from one instant to the next, it is usual to regard the rate of development as the rate at which the maximum pressure is reached. For convenience, the time between the moment of ignition and that of attainment of maximum pressure (time of explosion, *t*) is actually measured, but the rate of development of pressure is given by the reciprocal of this time, $1/t$.

FIG. 3.



When ignition takes place at the centre of a spherical vessel, the moment of attainment of maximum pressure synchronises with the moment at which the flame reaches the walls.* Hence the

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* Unless the speed of the flame is very slow. This was proved by Wheeler (J., 1918, **113**, 840) for mixtures of methane and air containing 7—11% of methane, by recording the time of fusion of screen wires (tinned copper wire of 0·025 mm. diameter) carrying an electric current and stretched near the wall of the explosion-vessel at a measured distance from the spark-gap. A similar method has been used in the present research, using mixtures of carbon monoxide and air, with the following results:

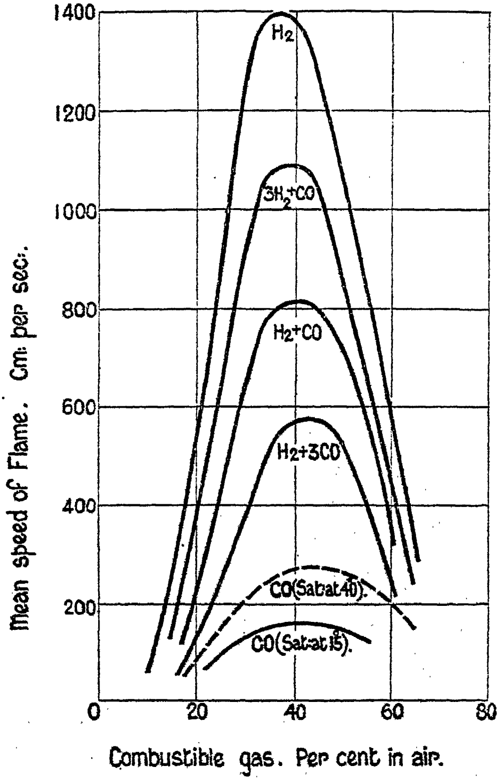
CO (%).	Time from ignition to maximum pressure (sec.).	Time taken for flame to reach wall of explosion-vessel (sec.).
	(*a*) Mixtures dried by calcium chloride.	
30·5	0·129	0·128
33·1	0·122	0·121
40·0	0·115	0·113
45·8	0·121	0·119
	(*b*) Mixtures saturated with water vapour at 15°.	
23·5	0·144	0·142
28·0	0·087	0·082
49·6	0·065	0·066

The times correspond within the limits of error of measurement of the speeds of the flames by the screen-wire method.

mean speed of the flame during its passage from the centre to the sides gives a direct measure of the "rate of development of pressure" as defined in the previous paragraph. This mean speed is r/t, where r is the radius of the sphere, which was 9·73 cm. in the present experiments. The equivalent value was used by Nägel (*loc. cit.*) for recording his results.

In Fig. 4, the rates of development of pressure are plotted against the compositions of the mixtures with air of H_2, $3H_2 + CO$, $H_2 + CO$, $H_2 + 3CO$, and CO. The dependence of the rate of development of pressure on the speed of the flame will be apparent if Fig. 4 be compared with Fig. 5, which records the speeds of propagation of flame during the uniform movement in a horizontal glass tube 2·5 cm. in diameter, the speeds being plotted against the compositions of the same series of mixtures as has been used in the present research. The mean speed of the flame in the sphere is about $2\frac{1}{2}$ times as great as that of the uniform movement in the glass tube.

FIG. 4.



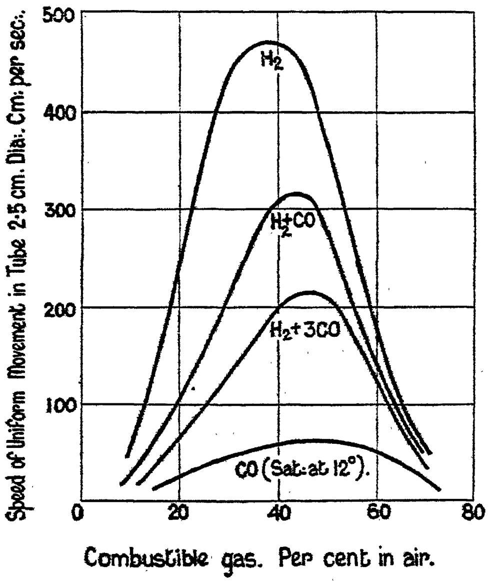
Application of the Law of Speeds.

To simplify the application of the law of speeds to the results recorded in Table I, those obtained with mixtures of carbon monoxide and air are not used in the first calculations, but are reserved until the effect of water vapour on the rate of development of pressure in carbon monoxide–air mixtures has been discussed. Instead of using hydrogen and carbon monoxide, therefore, as the two "standard" gases, hydrogen and the mixture

($H_2 + 3CO$) are used. Two vols. of hydrogen mixed with 1 vol. of ($H_2 + 3CO$) will yield a mixture of composition $3H_2 + CO$, whilst 1 vol. of hydrogen mixed with 2 vols. of ($H_2 + 3CO$) will yield a mixture of composition $H_2 + CO$.

The results of the calculations are shown in Fig. 6. In preparing this diagram, the times of explosion were first plotted against the compositions of the mixtures used as "standard." These curves are shown as continuous lines. From these curves, the "theoretical curves" for the mixtures $3H_2 + CO$ and $H_2 + CO$ were calculated by means of the law of speeds and are shown in the diagram in broken line. The values found experimentally were added to the diagram later. They show satisfactory agreement between observed and calculated values. Only the lower portions of the curves are shown in the diagram, since inclusion of all values found would have necessitated an excessive lengthening of the time scale.

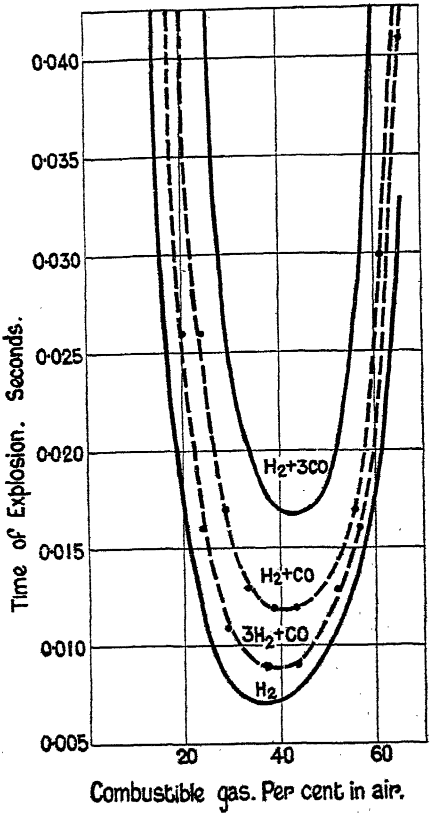
Fig. 5.



The Effect of Water Vapour on the Combustion of Carbon Monoxide.

In Part II of this series of papers (*loc. cit.*, p. 1252) it was shown that the speed of the uniform movement of flame in mixtures of carbon monoxide and air varied with the proportion of water vapour present. Some doubt, therefore, existed as to the correct value to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate, by means of the law of speeds, the speed of flame in complex mixtures containing carbon monoxide, unless the degree of saturation of the complex mixture by water vapour was known. It was shown, however, that when hydrogen, or an inflammable gas containing hydrogen, was present in the complex mixture in more than quite a small proportion, the speed of flame became independent of the concentration of water vapour, so that the speed of flame in such a complex mixture could be used as a basis from which an " effective " speed of flame in the mixtures of carbon monoxide and air could be calculated, and the value thus obtained could be used for further calculations. An alternative method for determining the " effective " speed of flame in a given mixture of carbon monoxide and air was described, this speed being the maximum obtainable with that mixture with the concentration of water vapour that had the optimum effect.

FIG. 6.



The same argument applies to the rate of development of pressure in complex mixtures of inflammable gases, containing carbon monoxide, ignited centrally in a spherical vessel. We have tested it experimentally, using a " maximum-speed mixture " of carbon monoxide and air, containing 48% of carbon monoxide, the amount of water vapour present being varied by varying the saturation-temperature. The explosion-vessel was installed within a heat-insulated wooden box, which also contained electric heater lamps. The pressure-gauge mirror and a portion of the gauge itself protruded from the enclosure.

The charge density was kept constant in these experiments, the bomb being filled at 15° and closed before being heated to the desired temperature. Sufficient water to ensure saturation at the experimental temperature was introduced into the bomb before filling it with the explosive mixture. The results are shown in Table II.

Time–pressure curves are reproduced in Fig. 7.

It will be seen that the rate of development of pressure tended towards a maximum when 6—7% of water vapour was present.

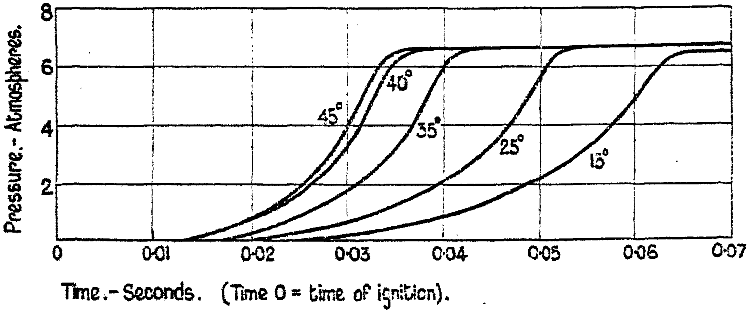
TABLE II.

The Influence of Water Vapour on the Rate of Development of Pressure in a Mixture of Carbon Monoxide and Air. (48% CO.)

Saturation temp.	Water vapour (% by vol.).	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure (sec.).
15°	1·7	0·025	0·065
25	2·9	0·020	0·053
35	4·8	0·017	0·043
40	6·2	0·012	0·038
45	7·9	0·014	0·037
50	9·7	0·014	0·038
55	12·0	0·015	0·037
65	17·3	0·015	0·037

This is rather more than is required to develop the maximum speed during the uniform movement of flame, when the explosive mixture is initially at atmospheric pressure.

FIG. 7.



Pressure development. Mixtures of carbon monoxide and air saturated with water vapour at different temperatures.

The value so obtained, 0·037 sec., for the "effective" time of explosion in the maximum-speed mixture of carbon monoxide and air, was now used as the standard, together with the corresponding value for the maximum-speed mixture of hydrogen and air, to calculate the times of explosion for the three mixtures $3H_2 + CO$, $H_2 + CO$, and $H_2 + 3CO$. The results are recorded, and compared with the experimentally determined values, in Table III.

TABLE III.

Inflammable gas	H_2.	$3H_2+CO$.	H_2+CO.	H_2+3CO.	CO.
Time of explosion (calc.) (sec.)	—	0·009	0·012	0·018	—
„ „ (obs.) „	0·007	0·009	0·012	0·017	0·037

The close agreement between the observed and calculated values affords decisive proof of the assumption that the "effective speed" of combustion of carbon monoxide is developed when a sufficient quantity of hydrogen is mixed with it, just as it is when a sufficiency of water vapour is present.

We pointed out, in our previous paper, that the results obtained by Bone and Haward (*loc. cit.*) for the rate of development of pressure in explosions of mixtures of carbon monoxide and hydrogen with air—results which the authors deemed to require an abnormal explanation—could be explained by the law of speeds. Bone, Newitt, and Townend (*loc. cit.*) have not accepted our explanation, regarding as "wholly fanciful" the assumption with regard to the "effective speed" of combustion of carbon monoxide which we have now proved to be correct, and have recorded the results of experiments intended to disprove it. Briefly, they have found that in certain explosions of the mixture $2CO + O_2 + 4N_2$, fired at an initial pressure of 50 atm., and at an initial temperature of 17—23·1°, what they term "the time in seconds taken for the attainment of maximum pressure" did not vary much whether the mixture were "dry," "undried," "moist," or "wet." Thus, they say: "There is practically no difference between the 'dry' and either the 'moist' or the 'wet' series; for in all these cases it amounted as nearly as may be to 0·18 second. In the 'undried' series (that is, when the water vapour present would probably not much exceed 1 in 2000) the time was somewhat shorter, namely, 0·13 to 0·15 second. It therefore seems clear that the presence of a very much smaller amount of water vapour sufficed to produce the optimum combustion conditions in our said experiments than was found necessary either by H. B. Dixon for the fastest propagation of detonation through $2CO + O_2$ mixtures at ordinary pressures, or by Payman and Wheeler for the fastest inflammation of carbon monoxide–air mixtures also at atmospheric pressure."

Apparently, the assumption is made that the amount of water vapour required to produce the optimum combustion conditions in their experiments was attained with the "undried" mixtures and had been passed with the "moist" and the "wet." Assuming that in the "wet" experiments the gases were saturated at the initial temperature and pressure (23·1° and 50 atm.), there could have been no more than 0·06% of water vapour present. In view of the fact that, under similar conditions of combustion, the concentration of water vapour found to be most effective lies between 6 and 7%, the speed of flame in a given mixture of carbon monoxide and air being then nearly four times as great as when the mixture is roughly dried, it is not surprising that Bone, Newitt, and Townend noticed very little difference between their series of experiments.

On the other hand, the smallest proportion of hydrogen in the mixture used by Bone and Haward was 1·2% (in the mixture $1/12H_2 + 23/12CO + O_2 + 4N_2$), or 20 times as much as the greatest proportion of water vapour in the mixtures used by Bone, Newitt, and Townend, whose experiments, therefore, yield no information regarding the relative influence of water vapour and hydrogen upon the explosion of carbon monoxide–air mixtures at high pressures. It may here be pointed out that although the times given by these authors are recorded as the times taken for "the attainment of maximum pressure," they are actually the times that elapsed between (*a*) the first indication of a rise above the initial pressure and (*b*) the attainment of the maximum, for they did not determine the time of ignition. There is no evidence that the interval that elapsed between ignition and the first appearance of pressure was negligible in their experiments or was the same in every one of the series. There is ample evidence that, in the explosion of mixtures initially at atmospheric pressure, this interval is of considerable importance.

Confirmation of our results is given by the work of Fenning (*loc. cit.*), who measured the time taken from the moment of ignition to the moment of attainment of maximum pressure in explosions (at an initial pressure of 5·2 atm. and an initial temperature of 50°) with a series of mixtures similar to those used by Bone and Haward. In discussing the results of his experiments, Fenning comments on the marked effect of a small proportion of hydrogen on the rapidity of explosion of a carbon monoxide–air mixture. The effect could have been calculated from the law of speeds in the following manner: Under the conditions of Fenning's experiments, the shortest time of explosion of the mixture $2CO + O_2 + 3{\cdot}8N_2$, *viz.*, 0·0901 sec., was obtained when the mixture was completely saturated with water vapour, when it contained 2·38% by volume. The time of explosion with a "comparatively dry" mixture of the same composition (containing less than 0·05% of water vapour) was 0·2693 sec. The time of explosion of a mixture $2H_2 + O_2 + 3{\cdot}8N_2$ was 0·0074 sec. From these values, the times of explosion for blends of the hydrogen–air and carbon monoxide–air mixtures can be calculated by the law of speeds, using alternatively the value for the "comparatively dry" and the "saturated" carbon monoxide–air mixture. The calculations are shown graphically in Fig. 8, in which the times of explosion are plotted against the compositions of the blends, the upper and lower curves being obtained when the values for the times of explosion in the dry and saturated carbon monoxide–air mixtures, respectively, are used. It is clear that the times of explosion of the blends used by Fenning should lie on a curve intermediate between the two calculated curves. That they do so is shown in the diagram by the insertion of his experimental values (*loc. cit.*, p. 351) as points.

To emphasise the importance of the presence of water vapour on the rate of development of pressure on explosion of mixtures of carbon monoxide and air, three series of experiments have been carried out, each covering a full range of mixtures between the limits of inflammability, with different concentrations of water vapour in each series. For the first series, the mixtures were roughly dried by passing them through calcium chloride tubes. For the second, they were saturated with water vapour at 15°, the results being recorded in Table I. For the third, they were saturated with water vapour at 40°, this being the temperature at which the optimum effect is produced. The values for the mean speeds of flame obtained in the last series of experiments may be taken as the "effective" values for the rate of development of pressure in carbon monoxide-air mixtures. They have been plotted as a broken line in Fig. 4. The results of the first and third series of experiments are recorded in Table IV.

FIG. 8.

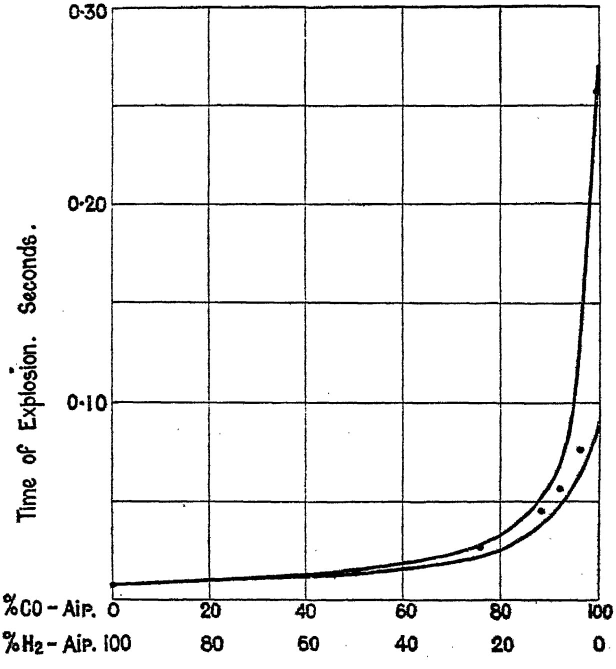


TABLE IV.

The Rate of Development of Pressure. Mixtures of Carbon Monoxide and Air.

Carbon monoxide, %.	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure, *t* (sec.).	1/*t*.	Mean speed of flame (cm./sec.).
(*a*) Mixtures dried by calcium chloride.				
19·4	0·105	0·337	3·0	30
24·9	0·054	0·150	6·7	65
30·5	0·048	0·129	7·7	75
33·1	0·050	0·122	8·2	80
40·0	0·042	0·115	8·7	85
45·8	0·046	0·121	8·3	80
49·6	0·048	0·136	7·3	70
(*b*) Mixtures saturated with water vapour at 40°.				
18·4	0·063	0·218	4·6	40
21·8	0·038	0·096	10·4	100
23·7	0·035	0·080	12·5	120
24·1	0·030	0·076	13·2	130
26·7	0·027	0·058	17·2	170
31·0	0·018	0·047	21·3	210
34·5	0·014	0·041	24·4	240
38·3	0·014	0·038	26·3	260
46·1	0·014	0·037	27·0	270
48·3	0·013	0·038	26·3	260
53·3	0·015	0·040	25·0	250
59·1	0·017	0·045	22·0	220
64·3	0·023	0·062	16·1	160

The experiments recorded in this paper form part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to utilise the results.

DEPARTMENT OF FUEL TECHNOLOGY,
SHEFFIELD UNIVERSITY.

[*Received, September* 11*th*, 1926.]

XLVIII.—*The Movement of Flame in Closed Vessels: After-Burning.*

By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER.

WHEN an explosive gaseous mixture is ignited at some point within a closed vessel, the speed at which the flame begins to spread * is compounded of the speed at which the inflammation is propagated, *i.e.*, is communicated from layer to layer of the mixture, and the speed at which the portion of the mixture about to be burnt moves under the expansive force of the portion already burning. Unless the speed of propagation of flame is very rapid, or the vessel very small, the unburnt mixture ahead of the flame-front at first moves freely without being appreciably compressed. A time comes, however, when, owing to the nearness of the walls of the vessel, the unburnt mixture ahead of the flame-front can no longer move freely. Its movement slackens until it ceases, the whole of the mixture between the flame-front and the walls of the vessel being compressed meanwhile, and, eventually, the direction of movement tends to be reversed. The movement of the flame is affected by this slackening of movement of the unburnt mixture, an appreciable retardation of its speed occurring as the walls of the vessel are approached (see *Fuel*, 1925, 4, 356).

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* The effect of any initial impetus that may be given by the source of ignition employed is here ignored.

This behaviour of the flame is illustrated in Fig. 1, Plate I, which shows a photographic record, taken on a rapidly revolving drum, of the flame in a 58·4% mixture of carbon monoxide and air moving away from the point of ignition at the centre of a sphere of glass, 9 cm. in diameter. In taking this and similar photographs reproduced in this paper, the outside surface of the sphere was covered with a layer of dead-black paint except for a horizontal slit, 3 mm. wide, facing the camera. The lens was focussed on a vertical plane passing through the point of ignition at right angles to the axis of the lens, and the sensitised paper can be regarded as moving vertically downwards. There is thus obtained a time–distance graph of the movement of the flame-front across the slit in either direction from the centre to the sides of the sphere. The speed of travel of the paper was recorded by photographing on it the sparks produced at the mercury contacts of an electrically-maintained tuning-fork of 100 frequency. The limits of the vessel are indicated on the photograph by the vertical parallel lines drawn thereon. It will be seen that the flame travelled from the spark at a uniform speed until within 1 cm. of the walls of the vessel, when a gradual retardation began.

It will be convenient to designate these two chief phases in the propagation of flame within a closed vessel, which are exhibited whatever the shape of the vessel, as Phase I and Phase II. During Phase I, which is of far longer duration when the vessel is of large volume, the speed of the flame when ignition is at the centre of a sphere, is nearly uniform. During Phase II the speed gradually decreases.

It will be understood that during Phase I the proper motion of the flame and that of the unburnt mixture ahead of the flame-front have the same direction, the unburnt mixture being moved freely as though it were not enclosed. During Phase II, the direction of motion of the flame and of the mixture may be opposed and combustion proceeds under an enhanced, and increasing, pressure which the mixture began to experience after Phase I of the propagation of flame had come to an end. Even the most sensitive pressure-gauge, without appreciable "lag," attached to the wall of the vessel, does not begin to register pressure until Phase I of the propagation of flame has ceased. This will be demonstrated in another communication.

We are particularly concerned in the present investigation with the behaviour of the flame during Phase II, and with the condition then obtaining of the products of combustion of Phase I. In our study thereof we have employed mainly the method of "snap-shot" photography previously described (J., 1925, **127**, 764), using carbon monoxide as the inflammable gas.

Explosions within a Sphere.—The series of photographs on Plate II was taken at successive stages during the explosion of a mixture of carbon monoxide and air containing 32·35% of carbon monoxide (corresponding almost to $2CO + O_2 + 3N_2$), saturated with water vapour at 15·5°, initially at atmospheric pressure. The explosion-vessel was a glass sphere, 9 cm. in diameter. Ignition was by a single secondary discharge at a 1·5 mm. spark-gap between platinum electrodes at the centre of the sphere. The photographs were taken on a vertical plane through the spark-gap. Each exposure lasted 1·67 millisecs., except that for photograph No. 12, which lasted 3·69 millisecs. For the purpose of reproduction, these photographs have been reduced to one-third of their original size. The boundary of the explosion-vessel is indicated by a white circle drawn on each photograph.

In the mixture used, flame travels at the same speed in all directions from the spark-gap. Its progress in a vertical plane can be traced in the photographs up to and including No. 6, where it can be seen touching the boundary of the vessel simultaneously at all points, the time taken for it to travel from the centre being 13·7 millisecs. It will be observed that the central portion of the vessel has become re-illuminated and remains illuminated long after the flame has touched the walls. The area illuminated gradually decreases, and the luminosity diminishes in intensity but is still appreciable 77·7 millisecs. after ignition or about 64 millisecs. after the flame has reached the boundary.

The point to which we wish to direct particular attention is that the re-illumination at the centre of the vessel began before the flame had touched the walls. It began, in fact, as soon as, or just after, what we have termed Phase II of the propagation began. At this instant, photograph No. 5 shows the presence of (i) a spherical

PLATE I.

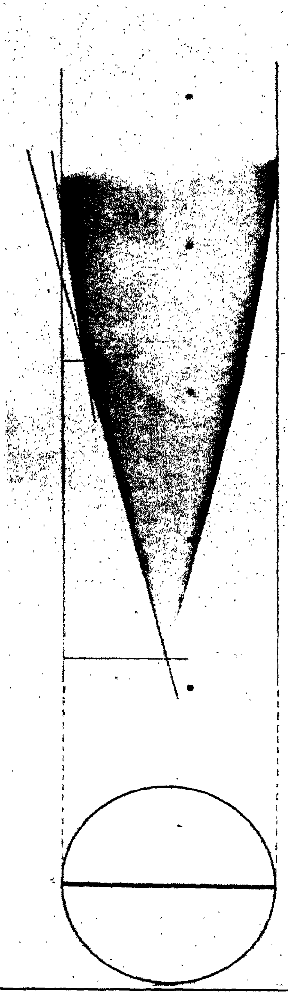


Fig. 1.

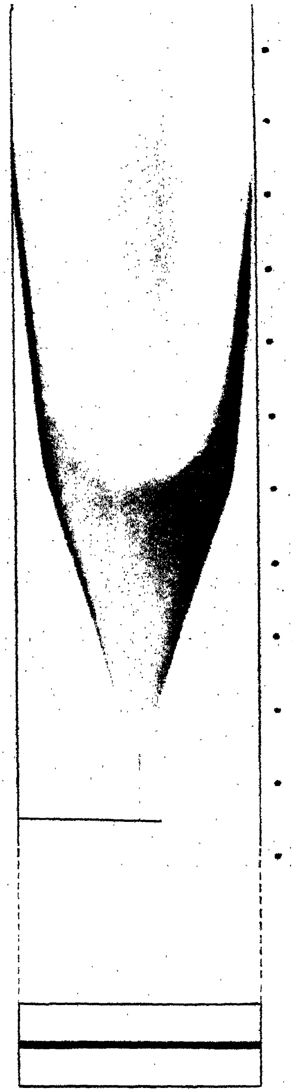
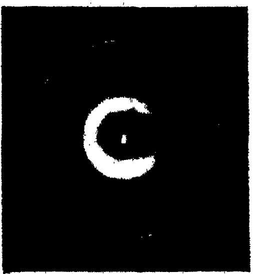


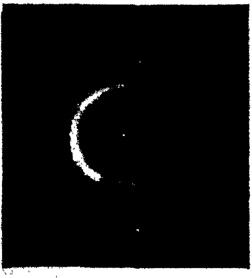
Fig. 2.

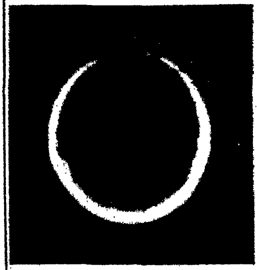
[*To face page* 312.]

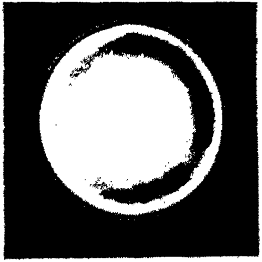
PLATE II.

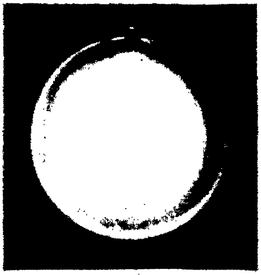
1. 3·4

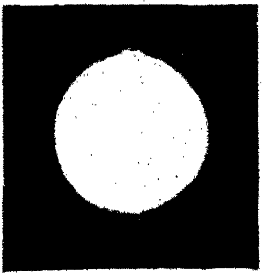

2. 4·6

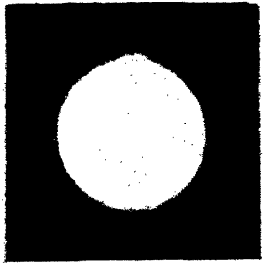

3. 6·3

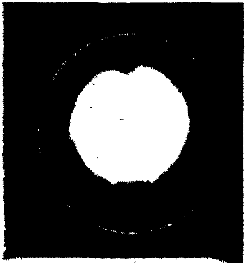

4. 9·2

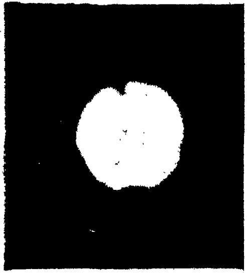

5. 11·4

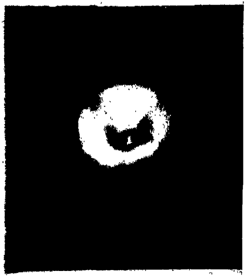

6. 13·7


7. 16·5


8. 20·6


9. 34·3


10. 52·7


11. 71·0

12. 77·7

The figures below each photograph record the times after ignition, in milliseconds, at which the photograph was taken.

shell of unburnt mixture between the flame-front and the walls of the explosion-vessel (non-luminous); (ii) the flame-front (luminous); (iii) the products of combustion just behind the flame-front (faintly luminous); and (iv) the residual gases from Phase I (brightly luminous).

Explosions within a Cylinder.—When the explosion occurs within a cylinder, the two chief phases in the propagation of flame have rather different characteristics from those of the corresponding phases when the explosion-vessel is spherical, but they are perhaps more clearly defined.

The photograph reproduced in Fig. 2 on Plate I was obtained in the same manner as that shown in Fig. 1 and should be compared with it. The explosion-vessel was a horizontal cylinder, 6 cm. in diameter and 16 cm. long. A 21·8% mixture of carbon monoxide and air was ignited at the centre of the vessel. The photograph is a time–distance graph of the movement of the flame-front along the axis of the cylinder in either direction from the centre to the ends. Phase I, during which the speed of the flame-front along the axis of the cylinder accelerates, ends just after the flame-front travelling transversely from the point of ignition has reached the walls of the cylinder. During Phase II the speed of the flame-front, which is now travelling in either direction horizontally only, is considerably retarded. In a cylinder of larger diameter the speed of the flame during Phase I is nearly uniform.

The series of photographs reproduced on Plate III are of stages in the explosion of a 27·7% mixture of carbon monoxide and air in the same cylinder, ignition being at the centre. The mixture was saturated with water vapour at 18° and was initially at atmospheric pressure. The intervals after ignition at which the photographs were taken are recorded below them. Each exposure lasted 2 millisecs.

As in a spherical explosion-vessel, the flame begins to travel at a uniform speed in all directions from the spark-gap, but it soon becomes egg-shaped because of its tendency to travel towards the ends of the cylinder rather than towards the sides. Phase I came to an end in photograph No. 4, 20·5 millisecs. after ignition, and signs of re-illumination at the centre of the vessel are noticeable (in the original negative) in the next photograph, taken 4·1 millisecs. later. The luminosity is well marked in photograph No. 7, just before the flame reaches the ends of the cylinder, and persists during at least 40 millisecs. after the flame has reached the ends, ultimately assuming a distinctive shape.

Similarly, numerous series of experiments, with different explosive mixtures ignited at different points within closed vessels of various shapes, have all shown that, when the luminescence we have described occurs, its inception corresponds with the beginning of Phase II. When ignition of the mixture is central with respect to the walls of the containing vessel, the luminous zone is near the centre; when ignition is asymmetric, the luminous zone occupies a position nearly central with respect to the contour of the flame-front at the end of Phase I; when there is multiple ignition, there is a luminous zone in the neighbourhood of each point of ignition. The luminescence must therefore be exhibited by the residual gases from Phase I of the propagation of flame.

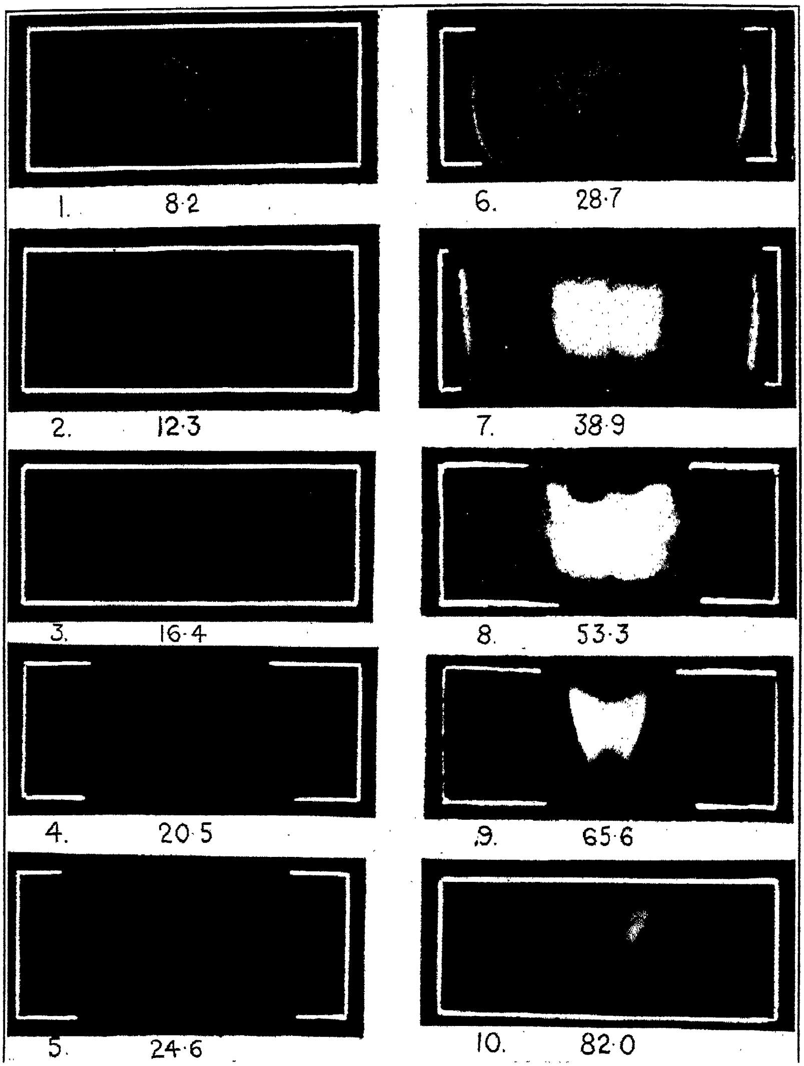
Three possible explanations of this luminescence suggest themselves. It may be due to (i) the re-association of dissociated molecules of carbon dioxide or steam; (ii) the dissociation of such molecules; or (iii) the completion of the combustion of molecules of (in the present instance) carbon monoxide that escaped being burnt whilst the flame was travelling.

Re-association. The zone of gas which exhibits the recrudescence of luminosity is that which was burnt during Phase I of the propagation of flame, *i.e.*, whilst combustion was taking place at comparatively low pressure and low initial temperature, for the unburnt mixture ahead of the flame was moving during this phase. Conversely, no luminosity (or, in some instances, which will be referred to later, but a faint luminosity) can be observed in the products of combustion formed during Phase II, which took place at comparatively high pressure and high initial temperature.

Re-association can only take place in the reactions under consideration on a falling temperature gradient, and the mass of gas in which it begins will be at a lower temperature than the remainder. But the residual gases from Phase I, at the time that they begin to show luminosity, cannot be falling in temperature, for they are being compressed owing to the combustion proceeding during Phase II. The luminescence begins long before any material cooling effect is possible. It is not normally displayed by the products of combustion of Phase II, which include those of the layer of mixture near the boundary of the vessel, when they begin to cool.

A reddish-yellow glow can often be observed after the flame in a closed vessel has completely expired. This glow can reasonably be assumed to be due to reassociation. We have not been able to photograph it, but its inception and duration could be studied by means of our apparatus, the camera being replaced by the eye, which is shielded during successively increasing intervals of time in a series of experiments with the same mixture. This dull glow is observed with mixtures which show no signs of luminescence,

PLATE III.



1. 8·2

2. 12·3

3. 16·4

4. 20·5

5. 24·6

6. 28·7

7. 38·9

8. 53·3

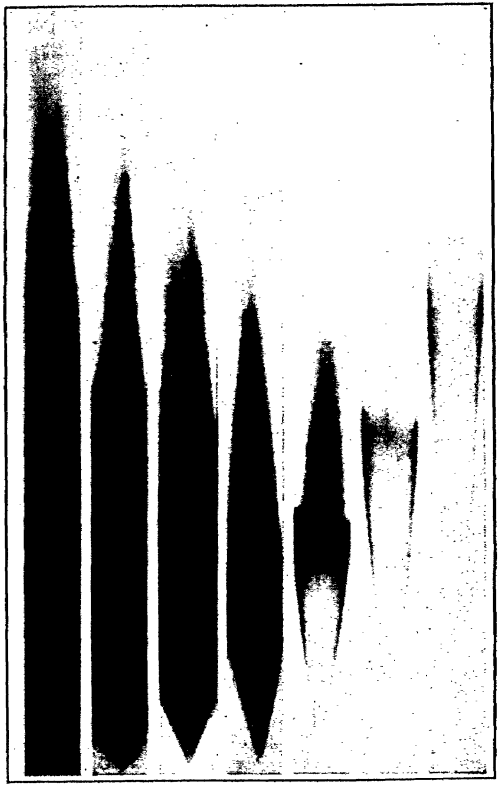
9. 65·6

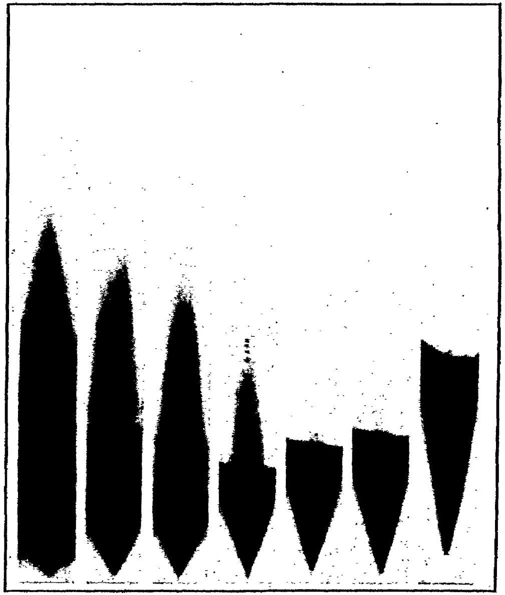
10. 82·0

The figures below each photograph record the times after ignition, in milliseconds, at which the photograph was taken.

[*To face page* 314.]

PLATE IV.





e.g., $2CO + O_2 + 4CO_2$, the calculated flame-temperature of which is about 2230° K., the amount of dissociation of carbon dioxide being about 1·5%. It is quite distinct in character from the luminescence the cause of which we are now considering. This is markedly actinic and leaves an impression on the eye of brilliant whiteness.

Dissociation. We have shown that the luminescence begins before material cooling of the gases which exhibit it can have begun. Actually, it would seem that the luminous gases, when they first make their appearance, are at a higher temperature than the products of combustion just behind the flame-front (which is then passing through Phase II) and, after the flame has reached the boundary, they represent the hottest zone within the explosion-vessel (Hopkinson, *Proc. Roy. Soc.*, 1906, *A*, 77, 387). Confirmatory evidence of this is to be seen in the locus of the luminescence within the vessel. In a sphere, when ignition is central, its locus is above the centre of the vessel (Figs. 8—12, Plate II). In a horizontal tube, ignition being at the centre, the central zone of luminescence is banked on both sides, just as banks of warm and cold air occur in the atmosphere, the slant planes heeling over towards the denser medium. This is well illustrated in the last three photographs on Plate III.

The fact that the gases exhibiting the luminescence remain at the highest temperature removes the possibility that dissociation of carbon dioxide or steam is its cause. Such dissociation must be accompanied by the absorption of heat, not by its evolution.

We conclude, then, that the luminescence is due to the completion of the combustion, under increased pressure, of molecules of combustible gas that escaped being burnt whilst the flame was travelling. This is, we believe, the conception of the "after-burning" postulated by Sir Dugald Clerk to account for the "lost" pressure in the gas-engine cylinder when he states: "The explosion is complete when maximum pressure is attained. It does not follow from this that the combustion is complete; that is another matter. The explosion arises from the rapid spreading of the flame throughout the whole mass of the mixture, which may be called the inflammation of the mixture. More or less rapid inflammation means more or less explosive effect, but not complete combustion. The complete burning of the gases present may not occur until long after complete inflammation" (Dugald Clerk, "The Gas, Petrol and Oil Engine," Vol. I, p. 128. London, 1910). We propose to attach this meaning to the term hereafter, despite the fact that it has been used by other writers in a different sense.

After-burning.

If after-burning be the true explanation of the luminescence now described, it should be possible to decrease or augment its amount by providing more or less favourable conditions for combustion to take place whilst the flame is travelling.

The Effect of Concentration of the Reacting Gases.—A series of mixtures $2CO + O_2 + nO_2$, saturated with water vapour at 0° (*i.e.*, containing 0·63% by volume of water vapour), was fired in a sphere 9 cm. in diameter, ignition being at the centre. Photographic records of the explosions were obtained on a rapidly revolving drum in the manner already described. The secondary discharge that caused ignition was produced in an identical manner in each experiment, the current through the primary circuit of the induction-coil being adjusted to a constant value. The records show (*a*) the total time taken for the flame to travel, in a vertical plane, from the centre to the walls of the vessel, which may be termed the duration of the flame; and (*b*) the duration of the after-burning beyond that of the flame. The results are recorded in Table I.

TABLE I.

The Explosion of $2CO + O_2 + nO_2$ *in a Closed Vessel.*

(Mixtures saturated with water vapour at 0°.)

Value of *n*.	Duration of flame (centisecs.).	Duration of after-burning (centisecs.).
2	2·7	19·7
3	3·3	16·9
4	3·75	16·25
5	4·9	14·7
6	7·7	6·4
7	11·3	0·8
8	15·1	Nil.

The mixture $2CO + O_2 + 9O_2$ is near the lower limit of inflammability. It will be seen that with the mixture $2CO + O_2 + 8O_2$ the concentration of oxygen has enabled the carbon monoxide to be burnt sufficiently completely during Phase I of the propagation to prevent any after-burning outlasting the flame. In each instance the after-burning had its origin in the products of combustion during Phase I of the propagation of flame and began to be noticeable just after Phase II had begun. The products of combustion during Phase II showed no traces of after-burning.

Similarly, in the series $2CO + O_2 + nCO$, saturated with water vapour at 0°, the results recorded in Table II were obtained.

In these mixtures after-burning was evident, from the photographic records, in the products of combustion during Phase II. The photographs of series I and II, reduced in size, are reproduced

TABLE II.

The Explosion of $2CO + O_2 + nCO$ *in a Closed Vessel.*

(Mixtures saturated with water vapour at 0°.)

Value of n.	Duration of flame (centisecs.).	Duration of after-burning (centisecs.).
4	2·1	11·2
5	2·3	9·3
6	2·5	7·8
7	3·4	4·7
8	4·2	1·8
9	4·4	1·5
10	6·9	Nil.

on Plate IV. In each photograph, the boundaries of the vessel are at the cut sides of the strip of sensitised paper, and the point of ignition is at the centre of the bottom edge.

In each series of mixtures, the duration of the after-burning clearly corresponds with the speed of propagation of the flame, being greater the greater the speed. For a given speed of flame, the duration of after-burning is less with excess of carbon monoxide than with excess of oxygen, as would be expected from considerations of mass-action. It should be noted that the duration of the after-burning is not necessarily a measure of its amount, although duration and intensity (as judged by the density of the photographic image) appear to be correlated in such series of mixtures as those recorded in Tables I and II.

The amount of gas burnt in accordance with Phase I of the propagation of flame also depends on the speed, for Phase I extends over a greater distance within the vessel the greater the speed. It can be said, therefore, that the amount of after-burning is dependent on the extent to which the propagation of flame takes place in accordance with Phase I.

The Effect of Water Vapour.—The duration of after-burning in mixtures of carbon monoxide and air or oxygen decreases rapidly as the amount of moisture present is increased. Now in a given mixture of carbon monoxide and air the presence of water vapour increases the speed of propagation of the "uniform movement" of flame, the optimum quantity being about 6% (W. Shepherd, quoted by Payman and Wheeler, J., 1923, **123**, 1253), and therefore should, according to the experiments just described, allow of greater facility for after-burning. The results for a mixture $2CO + O_2 + 4N_2$ are recorded in Table III.

The mixtures were saturated with water vapour at different temperatures, the initial pressure in each instance being atmospheric. The total mass present grew less, therefore, as the temperature rose, and the proportion of the mixture $2CO + O_2 + 4N_2$

TABLE III.

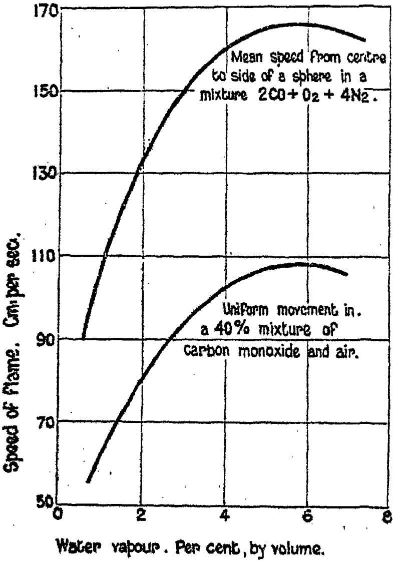
The Explosion of $2CO + O_2 + 4N_2$ *in a Closed Vessel.*

(Mixtures saturated with water vapour at different temperatures.)

Saturation temp.	Water vapour, %.	Duration of flame (centisecs.).	Duration of after-burning (centisecs.).
0°	0·63	5·1	15·8
5	0·85	4·7	15·1
10	1·21	4·0	15·2
15	1·68	3·6	15·0
20	2·31	3·2	14·1
25	3·13	3·0	13·7
30	4·20	2·8	13·2
35	5·55	2·7	11·6
40	7·28	2·8	10·4
45	9·47	2·8	9·7

in the mass grew less as the moisture content increased. A graph (Fig. 3) relating percentages of water vapour in the mixture with the mean speed of the flame from the centre to the side of the explosion-vessel bears a close resemblance to that obtained for the uniform movement of flame in a 40% carbon monoxide–air mixture, as determined by Shepherd for a tube 2·5 cm. in diameter (*loc. cit.*), and, as with the uniform movement, shows that the optimum amount of water vapour to develop the full speed of the flame under the conditions of experiment was about 6%.

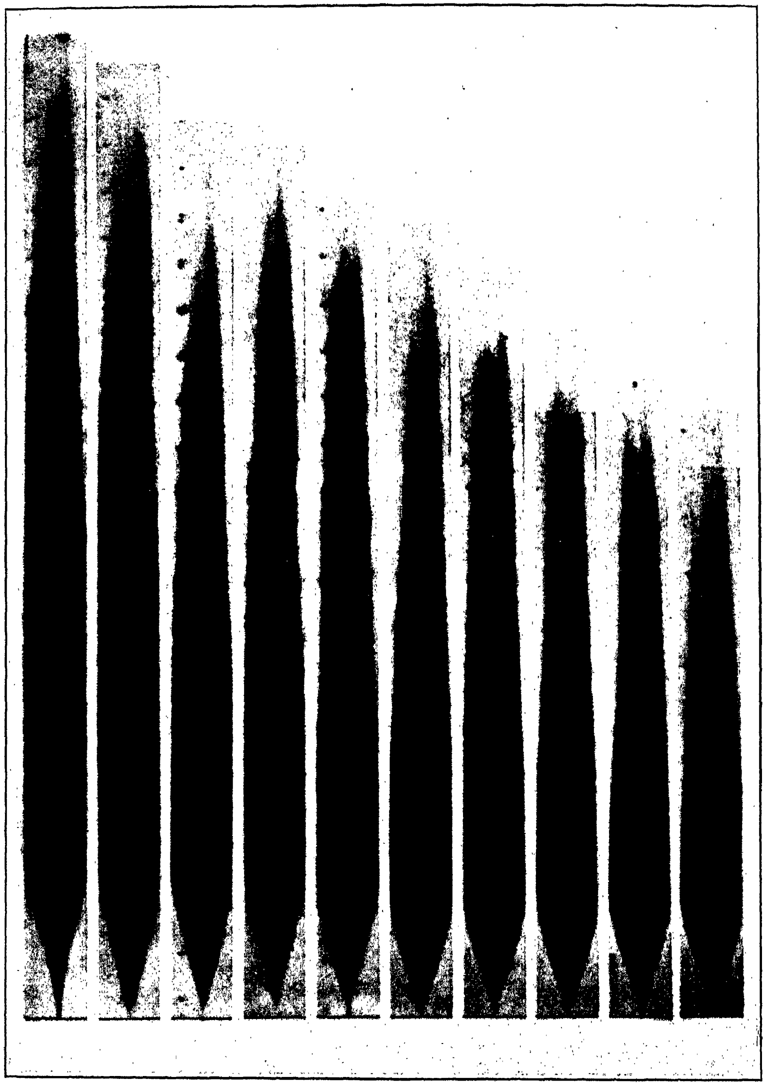
FIG. 3.



The records from which the values recorded in Table III were obtained are reproduced in Plate V. It will be seen that, despite the fact that the mean speed of the flame increased, both the duration and intensity of the luminescence decreased markedly as the moisture-contents of the mixtures increased. This effect we ascribe to the greater ease of combustion of the carbon monoxide during Phase I of the propagation of flame, due to the presence of the water vapour, there being in consequence less residual combustion or "after-burning."

The Effect of Diluent Gases.—Series of experiments were made in which different diluent gases, nitrogen, argon, and helium, were

PLATE V.



[*To face page* 318.]

added to the basic mixture $2CO + O_2$ in the same proportions, in order to vary the speed of flame without altering the relative concentrations of the combining gases. In each series, the proportion of water vapour was varied by saturating the mixtures at known temperatures. The results are recorded in Table IV.

TABLE IV.

The Explosion of $2CO + O_2 + 4X$ *in a Closed Vessel.*

Duration of (a) *Flame and* (b) *After-burning* (*centiseconds*).

Saturation temp.	Water vapour %.	$X = N_2$.		$X = A$.		$X = He$.	
		(a).	(b).	(a).	(b).	(a).	(b).
0°	0·63	5·1	15·8	3·4	20·3	2·1	16·6
5	0·85	4·7	15·1	3·2	19·2	2·1	16·2
10	1·21	4·0	15·2	2·9	18·4	1·8	14·9
15	1·68	3·6	15·0	2·6	17·6	1·55	14·55
20	2·31	3·2	14·1	2·4	17·2	1·5	13·6
25	3·13	3·0	13·7	2·2	16·1	1·3	13·2
30	4·20	2·8	13·2	2·1	16·0	1·15	13·2
35	5·55	2·7	11·6	2·0	15·1	1·1	12·9
40	7·28	2·8	10·4	2·0	14·1	1·2	12·3
45	9·47	2·8	9·7	2·0	11·6	1·3	10·7

Similarly, dilution of the basic mixture $2CO + O_2$ was effected by the participants in the equilibrium $2CO + O_2 \rightleftharpoons 2CO_2$, with the results shown in Table V.

TABLE V.

The Explosion of $2CO + O_2 + 4Y$ *in a Closed Vessel.*

Duration of (a) *Flame and* (b) *After-burning* (*centiseconds*).

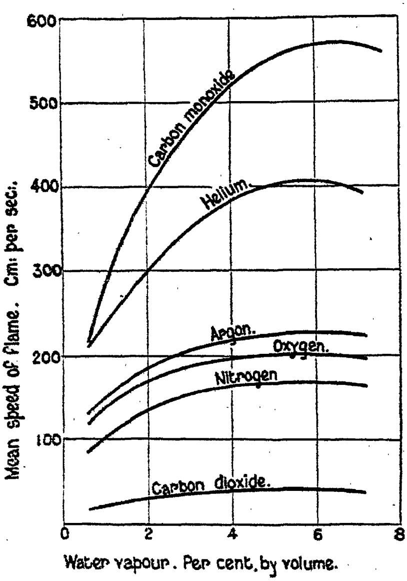
Saturation temp.	Water vapour %.	$Y = CO$.		$Y = O_2$.		$Y = CO_2$.	
		(a).	(b).	(a).	(b).	(a).	(b).
0°	0·63	2·1	11·2	3·75	16·25	23·3	11·5
5	0·85	1·8	11·3	3·3	16·3	20·4	11·0
10	1·21	1·45	10·35	3·0	16·0	(Not determined.)	
15	1·68	1·25	9·85	2·8	15·0	15·9	Nil.
20	2·31	1·1	9·3	2·6	14·0	13·9	„
25	3·13	0·95	9·3	2·5	13·5	12·7	„
30	4·20	0·85	9·15	2·4	12·8	12·5	„
35	5·55	0·8	8·9	2·2	12·8	11·3	„
40	7·28	0·75	7·95	2·3	11·5	11·75	„
45	9·47	0·8	7·4	2·3	10·5	11·8	„

From these series of experiments, we can form some judgment as to the effects of the various factors that influence the transference of heat during and after the propagation of flame, on flame-speed, and on the duration of after-burning.

The effect on flame-speeds can be studied by means of graphs

(Fig. 4) relating mean speeds of flame (measured from the centre to the side of the explosion-vessel) with percentages of water vapour in the different mixtures. As with the uniform movement of flame (Coward and Hess, quoted by Payman and Wheeler, Faraday Society Discussion, June 14th, 1926), the dependence of the flame-speed on the specific heat of the diluent gas and on its conductivity is readily apparent in the series of mixtures. The most striking comparison lies, however, in the effect of increasing the concentration of water vapour when excess of either of the two reacting gases, carbon monoxide and oxygen, is used as diluent. The effect is much more marked when carbon monoxide is in excess, although, as with all the diluents, the same optimum concentration of water vapour is indicated. The extent to which the reactivity of carbon monoxide is dependent on the presence of water vapour is thus strikingly displayed.

Fig. 4.

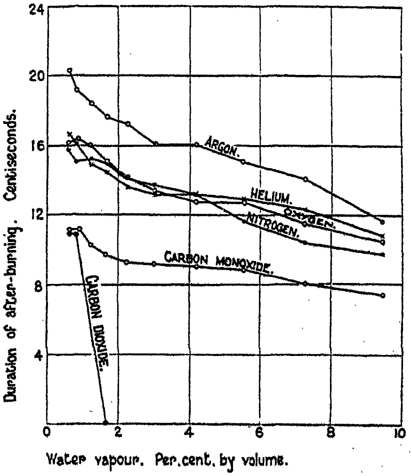


As regards the duration of after-burning, it will be understood that the records given are of the after-burning subsequent to the flame reaching the walls of the explosion-vessel, whereas we have shown that indications of after-burning begin before the flame reaches the walls. It is conceivable, in fact probable, that the inception of after-burning in the series of experiments recorded in Tables IV and V has varied with the character of the diluents X and Y. We cannot, from our present records, form an absolute estimate of the extent of variation in the time of inception of after-burning with the different mixtures (it appears to begin just after Phase II of the propagation begins); but, since by far the greater proportion of the after-burning occurs subsequent to the flame reaching the walls of the explosion-vessel, comparison of the figures recorded in Tables IV and V should serve our purpose.

It can be assumed that the amount of after-burning (residual combustion), as gauged by its duration, might be dependent upon (*a*) the degree of incompleteness of combustion during the propagation of flame, and (*b*) the facility afforded for the residual combustion to proceed. Any factor that would tend to accelerate the residual combustion would shorten its duration, and might increase its intensity.

In the several series of experiments that we have carried out, by progressively increasing the concentration of water vapour up to the optimum for the combustion of carbon monoxide, we have provided, with each diluent gas, a gradually increasing facility for completeness of combustion during the propagation of flame. By studying the general trend of variation in the duration of after-burning throughout each series, we should therefore be able to gauge the relative effect of the presence of each diluent gas in accelerating or retarding the residual combustion, as distinct from its original influence on the completeness of combustion during the propagation of flame. In Fig. 5, the duration of the after-burning, beyond that of the flame, is plotted against the proportion of water vapour in the mixtures for each of the series $2CO + O_2 + 4X$ (or 4Y).

FIG. 5.



All the photographs from which the records in Tables IV and V were obtained were taken on Lumière paper from the same source of supply. They were developed during the course of one day, each being treated during 150 secs. in a bath of standard developer at a uniform temperature of 5°. The duration of after-burning can be measured accurately within 0·1 centisec.

A fact to be noted is that no support can be obtained for the suggestion that the luminescence that we ascribe to after-burning may be due to the recombination of dissociated carbon dioxide or steam molecules. The amount of dissociation would be greatest with those mixtures having the highest "flame-temperature." The duration of after-burning is, for all concentrations of water vapour, greatest with the argon mixtures (calculated flame-temperatures, 3520° K.), and is markedly greater than with the helium mixtures, for which the calculated flame-temperatures are the same. Moreover, the duration of after-burning with the helium mixtures is nearly the same as with the nitrogen and the oxygen mixtures, although the calculated flame temperatures for these are much lower (2890° K.). With the carbon monoxide mixtures (calculated flame temperatures, 2890° K.), the duration of after-burning is throughout considerably the shortest. With the carbon dioxide mixtures, in which the speed of flame is exceptionally slow (calculated flame-temperatures, 2230° K.), there is no after-burning when the concentration of water vapour exceeds about 1·5%, but with the lowest concentration (0·63%) it is nearly as long as with carbon monoxide.

We are unable at present to offer a complete explanation of the effect of argon. We have noticed that, not only is the duration of the after-burning longest when this gas is the diluent, but its actinic effect, and that of the flame also, is greatest. In another research, in which the propagation of flame in mixtures of hydrogen and air is being studied, the substitution of argon for the nitrogen has been found greatly to affect the actinic power of the flames. It may well be that in these experiments the high actinic value of the luminescence when argon is present enables it to be registered photographically for a longer period than in the other series.

This leads us to a consideration of the relative actinic effects of the luminescence and of the flames. The photographs reproduced on Plates II and III show, what is a general observation, that the luminescence has a greater effect on a photographic plate than the flame itself. It is true that the flame is moving whilst it is being photographed, whereas the luminescence is nearly stationary, but, making allowance for this, the difference is so great as to suggest that different forms of radiation are being emitted during the two phenomena of flame propagation and after-burning. On the other hand, there is no evidence that the chemical reactions during the after-burning differ in character from those during the propagation of flame. On the contrary, it is clear (see Fig. 5) that the combustion of carbon monoxide during the after-burning is facilitated by the presence of water vapour just as it is during the propagation of flame. The actinic power of the luminescence may therefore be due solely to the fact that the combustion of the residual carbon monoxide is proceeding at a high temperature and pressure. This question can perhaps be determined by spectroscopic methods of research, which we now have in hand. The research is being continued, also, to include the combustion of gases other than carbon monoxide.

Our thanks are due to the Safety in Mines Research Board for permission to publish this paper.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD.

[*Received, September 30th,* 1926.]

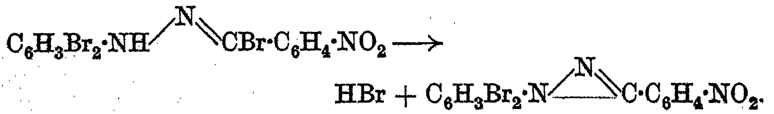
XLIX.—*The Reduction of* o-*Nitrophenyl*iso*diazomethanes.*

By Frederick Daniel Chattaway and Arthur John Walker.

In previous papers it has been shown (J., 1925, **127**, 1687, 2407) that the direct action of halogens upon the nitrobenzaldehydephenylhydrazones leads to substitution in the ω-position; *e.g.*,

$$C_6H_5{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2 \xrightarrow{3Br_2} C_6H_3Br_2{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2.$$

Of these ω-halogen derivatives, those derived from *o*-nitrobenzaldehydephenylhydrazone behave in an anomalous manner, easily splitting off halogen acid and forming explosive compounds. The α-hydrogen and the ω-halogen atom are eliminated in this change, which is simply accounted for by assuming the formation of a three-atom *iso*diazomethane ring thus:



A number of these *o*-nitrophenyl halogenophenyl *iso*diazomethanes have been described (*loc. cit.*, p. 2410) and the present paper is concerned with a further study of their properties, and notably of the products they yield on reduction.

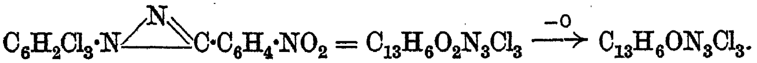
They are all well-crystallised, yellow substances which can be kept indefinitely at the ordinary temperature without change but explode with great violence when heated. In hot solution, they suffer decomposition to a greater or less extent. Those containing three halogen atoms in the nucleus are markedly more stable than those with less halogen. They are stable towards acids, and show feebly basic properties, dissolving in concentrated hydrochloric acid, for example, and being reprecipitated on dilution. When hydrogen chloride is passed into their dry ethereal solutions, colourless addition compounds are precipitated. These readily lose hydrogen chloride and revert to the original compounds on exposure to air, or on moistening with water.

They are all rapidly decomposed by alcoholic potash, or alcoholic ammonia, yielding as one of the products a halogen-substituted benzene (*e.g.*, *o*-nitrophenyl-2 : 4 : 6-trichlorophenyl*iso*diazomethane yields 1 : 3 : 5-trichlorobenzene).

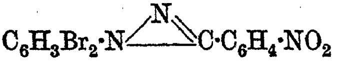
On oxidation with permanganate they yield *o*-nitrobenzoic acid.

Behaviour on Reduction.—When the *o*-nitrophenyl halogenophenyl *iso*diazomethanes are boiled for some time with alcohol they undergo reduction to almost colourless compounds, the alcohol being simultaneously oxidised to acetaldehyde. The same reaction can more conveniently be effected by the action of stannous chloride in the cold.

The products are well-crystallised compounds, and their analysis shows that in every case they are formed by loss of one atom of oxygen from the original *iso*diazomethane; *e.g.*,



$$C_6H_2Cl_3\cdot N\overset{N}{\triangle}C\cdot C_6H_4\cdot NO_2 = C_{13}H_6O_2N_3Cl_3 \xrightarrow{-O} C_{13}H_6ON_3Cl_3.$$

For the study of the constitution of these products, the one derived from *o*-nitrophenyl-2 : 4-dibromophenyl*iso*diazomethane,  $C_6H_3Br_2\cdot N\overset{N}{\triangle}C\cdot C_6H_4\cdot NO_2$ (which is typical of the series), was selected.

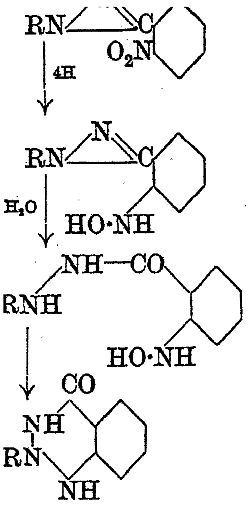
Prepared by reducing the *iso*diazomethane with stannous chloride, it crystallises in colourless needles, m. p. 176°. Under reduced pressure, it can be distilled unchanged, and it is unaffected by hot concentrated mineral acids. The halogens do not attack it at the ordinary temperature. It is, however, decomposed by alcoholic potash, giving a deep red solution. If this be effected in presence of silver nitrate, an amorphous, spontaneously explosive compound is produced.

The great stability of the original reduction product suggests that the *iso*diazomethane ring has been broken, and a larger, and more stable ring formed, in which the nitrogen of the original nitro-group is probably included.

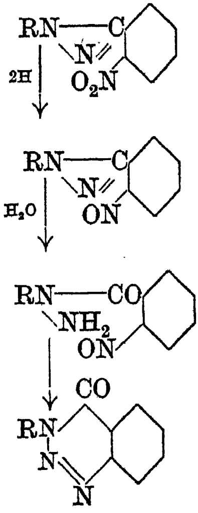
The compound still contains one oxygen atom, which is not removed on further reduction with tin and hydrochloric acid, indicating that this can no longer be attached to nitrogen, and is probably attached to carbon.

In representing the formation of such a compound, we may assume that reduction of the nitro-group occurs, and is followed by rupture of the three-atom ring by hydrolysis, the reduced nitro-group finally linking up to form the larger ring.

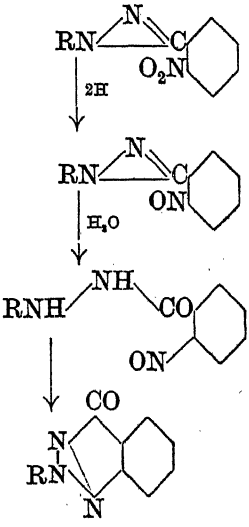
According to the extent to which reduction occurs in the nitro-group and the manner in which the three-atom ring is broken, we have the following possibilities ($R = C_6H_3Br_2$):



(I.) Dibromophenyl-dihydrobenztriazone.



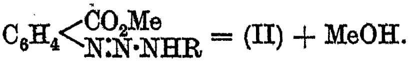
(II.) Dibromophenyl-benztriazone.



(III.) *cycloazi*-Dibromophenylbenztriazone.

The first of these possibilities is excluded by the fact that the compound in question forms no acetyl derivative, and is unaffected by nitric or nitrous acid. Further, the minimum quantity of stannous chloride required for its production does not correspond with that required by this formula.

The second (II) of these was synthesised directly for comparison, by the method of Mehner (*J. pr. Chem.*, 1901, **63**, 279) from methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate :

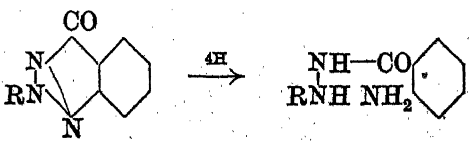


$$C_6H_4{<}{}^{CO_2Me}_{N:N\cdot NHR} = (II) + MeOH.$$

The product proved *not* to be identical with the reduction product of the *iso*diazomethane, and constitution (II) is therefore excluded.

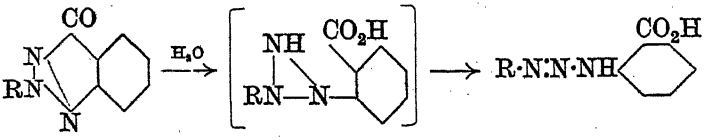
Formula (III) has been adopted, since it accounts in a satisfactory way for the products obtained when the compound is subjected to further reduction, and when it is decomposed by alkalis.

Reduction. On reduction in the cold with tin and hydrochloric acid, it yields o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine* :



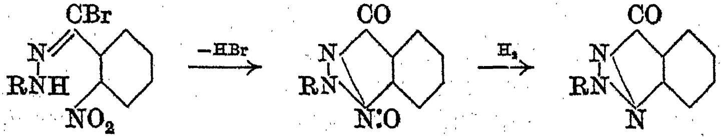
which yields dibromophenylhydrazine and anthranilic acid on hydrolysis and is identical with the compound obtained by reducing *o*-nitrobenzoyl-2 : 4-dibromophenylhydrazine.

Decomposition by potash. By the action of alcoholic potash in the cold, the compound yields 2 : 4-*dibromodiazoaminobenzene-2′-carboxylic acid*[*] identical with the acid obtained by coupling dibromobenzenediazonium chloride with anthranilic acid. The decomposition[†] may be represented:



The constitution of the reduction product is therefore well established, and there is no doubt that those obtained from similar *iso*diazomethanes are analogously constituted.

The preceding work suggests that an *alternative to the* iso*diazomethane structure* ought to be considered. By assuming an *iso*diazomethane structure for the explosive compounds we have a simple explanation of their formation from the ω-halogen derivatives (see p. 323). On the other hand it has to be borne in mind that the power to form these explosive compounds is limited to those ω-halogen derivatives containing the nitro-group in the ortho-position. This suggests that the reaction may be one in which the nitro-group (by virtue of its ortho-position) actually takes part, and the subsequent reduction to benztriazones lends support to this view. On this alternative theory the explosive compound might be represented as a nitrosoazi-compound, which would naturally pass into the triazone on reduction,



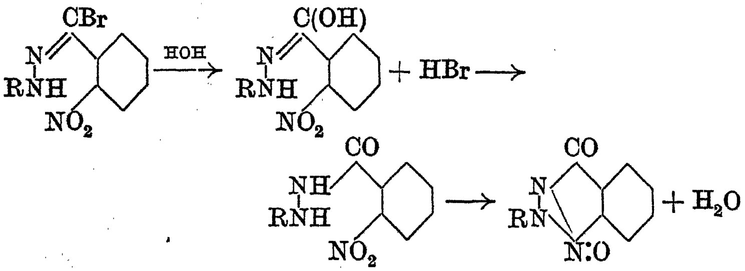
(explosive compound)
(alternative structure)

the formation from the ω-halogen derivative taking place by hydrolysis of the halogen, and ring closure involving the nitro-group :

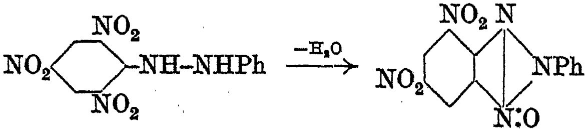
---

[*] At the same time, an isomeric acid is produced, which is probably the corresponding aminoazo-compound.

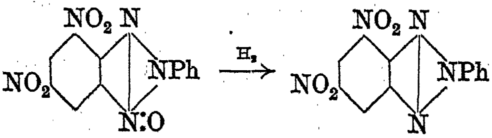
[†] The highly explosive compound formed when this is carried out in presence of silver nitrate (p. 328) may be a derivative of the intermediate compound (not isolated), written in brackets.



The work of Willgerodt (*J. pr. Chem.*, 1897, **55**, 375; compare also Werner and Stiasny, *Ber.*, 1899, **32**, 3266) on nitrohydrazobenzenes favours this interpretation. He finds that hydrazobenzenes containing a nitro-group in the ortho-position can lose water in the following way,



forming nitrosoazi-derivatives. These, like the explosive compounds here described, are easily reduced (by boiling alcohol) to the corresponding azimido-compounds.



EXPERIMENTAL.

Reduction of 1-2′ : 4′-*Dibromophenyl*-3-o-*nitrophenyl*iso*diazomethane to* cycloazi-*Dibromophenylbenztriazone* (III).—(a) *With alcohol.* 2 : 4-Dibromophenyl-*o*-nitrophenyl*iso*diazomethane (5 g.) was boiled under reflux with 100 c.c. of alcohol for 3—4 hours. The solution thus obtained was boiled for another hour, and a few c.c. were then distilled off. These contained acetaldehyde, detected by its smell, and by its action upon Fehling's solution, ammoniacal silver nitrate, and Schiff's reagent. The main bulk of the solution, on cooling, deposited colourless crystals of cycloazi-2 : 4-*dibromophenylbenztriazone*. Recrystallised from alcohol, in which it is moderately easily soluble, it forms long, colourless needles, m. p. 178° (yield, 3 g.) (Found: Br, 42·1. $C_{13}H_7ON_3Br_2$ requires Br, 42·0%).

(b) *With stannous chloride.* For the preparation of larger quantities, this method is more convenient. 2 : 4-Dibromophenyl-*o*-nitrophenyl*iso*diazomethane (10 g.) was ground to a paste with

60—70 c.c. of acetic acid, and 200 c.c. of concentrated hydrochloric acid added.

The whole formed a clear yellow solution, which was maintained at 10—15° while a solution of 15 g. (excess) of stannous chloride in 50 c.c. of concentrated hydrochloric acid was slowly run in with vigorous stirring. The reduction product, which meanwhile separated as a pale yellow precipitate, was washed with dilute hydrochloric acid and then with hot water and finally recrystallised from alcohol; m. p. 178° (yield, 7 g.).

General properties. The compound is remarkably stable, and when heated under reduced pressure above its melting point distils with only slight decomposition. It is insoluble in dilute mineral acids, but dissolves in hot concentrated sulphuric, hydrochloric, and nitric acids; from these solutions, it is precipitated unchanged by dilution.

It does not react with nitrous acid, and is recovered unchanged after 8 hours' boiling with acetic anhydride and a drop of sulphuric acid or with acetic anhydride and anhydrous sodium acetate. It is, however, decomposed by alcoholic potash, yielding a deep red solution (see p. 331).

When a solution of the compound in alcohol is warmed with a few drops of ammoniacal silver nitrate solution, and a little caustic potash, a black, amorphous precipitate is slowly formed. If this be touched with a glass rod, or in any way disturbed, under the supernatant liquid, it explodes sharply with great violence, invariably shattering the tube.

Analogous Reduction Products.—By the action of boiling alcohol, or of stannous chloride in the cold, other halogenophenyl-*o*-nitrophenyl*iso*diazomethanes yield reduction products, *cycloazi*-phenylbenztriazones, closely resembling the one described. For the sake of the additional analytical data which they afford, three of these were prepared and analysed.

cycloazi-p-*Bromophenylbenztriazone* was prepared from *p*-bromophenyl-*o*-nitrophenyl*iso*diazomethane by both methods. It crystallises from alcohol, in which it is moderately easily soluble, in pale yellow needles, m. p. 197° (Found : Br, 26·4. $C_{13}H_8ON_3Br$ requires Br, 26·5%).

cycloazi-2 : 4-*Dichlorophenylbenztriazone* was prepared from dichlorophenyl-*o*-nitrophenyl*iso*diazomethane by both methods. It exists in two polymorphic forms. The labile form separates from alcoholic solution in compact, yellow prisms, m. p. 167°; these, in contact with the mother-liquor, dissolve and the stable form appears as colourless needles, m. p. 157°. At the ordinary temperature, in contact with a saturated alcoholic solution, the yellow form slowly changes into the colourless (Found: C, 54·0; H, 2·6; N, 14·3; Cl, 24·2; *M*, in phenol, 272. $C_{13}H_7ON_3Cl_2$ requires C, 53·9; H, 2·5; N, 14·4; Cl, 24·3%; *M*, 292).

cycloazi-2 : 4 : 6-*Trichlorophenylbenztriazone* prepared from 2 : 4 : 6-trichlorophenyl-*o*-nitrophenyl*iso*diazomethane by both methods, crystallises from alcohol, in which it is only moderately readily soluble, in colourless needles, m. p. 258° (Found: C, 47·7; H, 2·1; N, 13·5; Cl, 32·4; *M*, in phenol, 300. $C_{13}H_6ON_3Cl_3$ requires C, 47·8; H, 1·9; N, 12·85; Cl, 32·6%; *M*, 326·5).

Synthesis of Isomeric Phenylbenztriazones for Comparison.—p-*Bromophenylbenztriazone* (II; R = *p*-C_6H_4Br). A solution of 3 g. (1 mol.) of methyl anthranilate in 5 c.c. (2·5 mols.) of concentrated hydrochloric acid and 30 c.c. of water was diazotised at 0° with 1·4 g. (1 mol.) of sodium nitrite. A solution of 3 g. of *p*-bromoaniline in dilute hydrochloric acid was added, and then excess of a cold solution of sodium acetate; methyl *p*-bromodiazoaminobenzene-*o*′-carboxylate slowly separated. It crystallised from alcohol, in which it is moderately easily soluble, in golden-yellow needles (yield, 4·5 g.), m. p. 120° (Found: Br, 24·9. Calc.: Br, 24·8%).

The conversion into p-*bromophenylbenztriazone* was effected by boiling for 2 hours with a mixture of 2 vols. of alcohol and 1 vol. of water; on cooling, the benztriazone separated in colourless crystals.

Recrystallised from alcohol, in which it is moderately easily soluble, it separated in colourless plates, m. p. 196°, which proved quite distinct in appearance and properties from the reduction product of *p*-bromophenyl-*o*-nitrophenyl*iso*diazomethane, m. p. 197°. A mixture of the two melted below 190° (Found: Br, 26·5. $C_{13}H_8ON_3Br$ requires Br, 26·5%).

2 : 4-*Dibromophenylbenztriazone* (II). Attempts to obtain methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate from methyl anthranilate and dibromoaniline by diazotising and coupling in the usual way were unsuccessful, as the addition of sodium acetate to the acid solution of diazonium salt and amine simply reprecipitated the amine (dibromoaniline or methyl anthranilate) unchanged.

This difficulty was overcome by employing acetic acid as solvent in the place of water: To 5 g. (1 mol.) of dibromoaniline, dissolved in 50 c.c. of acetic acid, were added 10 c.c. (5 mols.) of concentrated hydrochloric acid and the mixture was cooled to 0° and diazotised by adding a saturated aqueous solution of 1·4 g. (1 mol.) of sodium nitrite. The diazo-solution was then mixed with a cold solution of 3 g. (1 mol.) of methyl anthranilate in 20 c.c. of acetic acid and 5 c.c. of water. On adding an excess of anhydrous sodium acetate, the diazoamino-compound slowly separated. After ½ hour, the mixture was diluted considerably with water, and the methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate was filtered off and recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in bright yellow needles, m. p. 141° (Found: Br, 40·0. Calc.: Br, 39·9%).

The ester (1 g.) was heated at 100° for 2 hours in a sealed tube with 50 c.c. of alcohol and 10 c.c. of water (Mehner, *J. pr. Chem.*, 1901, **63**, 241). The *triazone* separated as a colourless solid when the cooled product was poured into water. It was crystallised from alcohol, in which it is moderately easily soluble, and from which it separates in compact prisms, m. p. 136° (Found: Br, 42·1. $C_{13}H_7ON_3Br_2$ requires Br, 42·0%).

The compound is quite distinct in appearance and properties from the reduction product of dibromophenyl-*o*-nitrophenyl*iso*diazomethane, m. p. 178° (see p. 327). On boiling for an hour with alcoholic potash it yielded, as the sole product of hydrolysis, 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid, m. p. 151° (see p. 332).

Reduction of cycloazi-2 : 4-*Dibromophenylbenztriazone to* o-*Aminobenzoyl*-2 : 4-*dibromophenylhydrazine.*—A solution of 5 g. of *cycloazi*-2 : 4-dibromophenylbenztriazone in 50 c.c. of boiling acetic acid was rapidly cooled with the addition of 40 c.c. of concentrated hydrochloric acid, so that a fine crystalline suspension was obtained. A considerable excess of granulated tin was added, and the whole kept at the ordinary temperature for 5 hours; the original solid had then completely dissolved. The solution was decanted from the tin, diluted with an equal volume of water, and extracted four times with 150—200 c.c. of ether. The ethereal layer was washed with water and dilute sodium carbonate solution, dried over potassium carbonate, and the ether distilled off. The colourless product, o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine*, exists in two polymorphic forms; when crystallised from alcohol, in which it is moderately easily soluble, it separates first in colourless needles, which in the solvent slowly transform to compact plates; both forms melt at 184°. Yield, 2 g. (Found: Br, 41·55; N, 11·2. $C_{13}H_{11}ON_3Br_2$ requires Br, 41·6; N, 10·9%).

The constitution of *o*-aminobenzoyl-2 : 4-dibromophenylhydrazine was determined by its hydrolysis to anthranilic acid and 2 : 4-dibromophenylhydrazine, and by its synthesis from *o*-nitrobenzoyl-2 : 4-dibromophenylhydrazine by reduction.

Hydrolysis. The substance, heated with concentrated hydrochloric acid in a sealed tube for 2 hours at 100°, yielded anthranilic acid, m. p. 144°, and 2 : 4-dibromophenylhydrazine; the latter was identified by conversion into its characteristic, bright red *o*-nitrobenzaldehydehydrazone, m. p. 205°.

Synthesis. β-o-*Nitrobenzoyl*-2 : 4-*dibromophenylhydrazine*, prepared by the Schotten-Baumann method from *o*-nitrobenzoyl chloride and dibromophenylhydrazine, crystallised from alcohol, in which it is moderately easily soluble, in yellow needles, m. p. 180° (Found: Br, 38·5. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·55%).

The reduction of this compound with tin in a cold mixture of acetic and hydrochloric acids yielded the same product, *o*-aminobenzoyl-2 : 4-dibromophenylhydrazine, as the reduction of *cycloazi*-dibromophenylbenztriazone, melting at 184° and crystallising in the same two polymorphic forms.

This identity was further established by the preparation and comparison of its mono- and di-acetyl derivatives. o-*Acetamidobenzoyl*-2 : 4-*dibromophenylhydrazine*, $C_6H_3Br_2\cdot NH\cdot NH\cdot CO\cdot C_6H_4\cdot NHAc$, prepared by the action of acetic anhydride alone upon *o*-aminobenzoyldibromophenylhydrazine in the cold, forms colourless needles, m. p. 210° (Found: Br, 37·3. $C_{15}H_{13}O_2N_3Br_2$ requires Br, 37·5%).

o-*Acetamidobenzoyl*-α-*acetyl*-2 : 4-*dibromophenylhydrazine*,

$$C_6H_3Br_2\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NHAc,$$

prepared by boiling *o*-aminobenzoyldibromophenylhydrazine with acetic anhydride and a drop of sulphuric acid, crystallises from alcohol, in which it is much more soluble than the monoacetyl derivative, in clusters of colourless needles, m. p. 184° (Found: Br, 34·2. $C_{17}H_{15}O_3N_3Br_2$ requires Br, 34·1%).

The Action of Potash on cycloazi-2 : 4-*Dibromophenylbenztriazone.*—A solution of 10 g. of *cycloazi*-dibromophenylbenztriazone in 150 c.c. of boiling alcohol was chilled to produce a fine crystalline pulp. A solution of 20 g. of caustic potash in 100 c.c. of alcohol and 5 c.c. of water was then added, and the whole kept at the ordinary temperature for 5—6 hours; the original crystals had then completely dissolved to give a deep red solution.

This solution contains the yellow potassium salt of 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid, and in addition, smaller quantities of the deep red potassium salt of another, more stable acid, of the same composition. The sparing solubility in aqueous alcohol of the former renders its isolation a comparatively easy matter.

To the red alcoholic solution was added a little more than its own volume of water; the potassium salt of dibromodiazoaminobenzene-2′-carboxylic acid then separated in an impure condition. It was redissolved in a small quantity of alcohol and again precipitated with an equal volume of water (yield, 2—3 g.). It may be recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in long, slender, pale yellow needles, m. p. 230—240° (decomp.). It is very sparingly soluble in water.

The free 2 : *4-dibromodiazoaminobenzene-2′-carboxylic acid*, prepared from the potassium salt by treatment with acetic acid, was recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in yellow needles which melt at 151°, decomposing with a sharp puff. The crystallisations were effected as rapidly as possible, as the substance easily decomposes on prolonged boiling (Found: C, 39·5; H, 3·4; N, 10·1; Br, 40·1. $C_{13}H_9O_2N_3Br_2$ requires C, 39·1; H, 3·9; N, 10·5; Br, 40·2%).

On reduction with zinc in acetic acid, it yielded anthranilic acid and 2 : 4-dibromoaniline. Its constitution was further confirmed by its synthesis direct from anthranilic acid and 2 : 4-dibromobenzenediazonium chloride. The coupling was effected without difficulty in aqueous solution, and the insoluble diazoamino-compound, after recrystallisation from alcohol, melted at 151° and proved to be identical with the compound obtained from *cycloazi*-dibromophenylbenztriazone.

The Isomeric Acid, $C_{13}H_9O_2N_3Br_2$.—The red mother-liquors remaining from the precipitation of potassium dibromodiazoaminobenzene-2′-carboxylate (see p. 331) were acidified with acetic acid, whereby a mixture of the free isomeric acids was precipitated as a brownish-red solid. This was separated, and the more easily soluble dibromodiazoaminobenzene-2′-carboxylic acid extracted with 100 c.c. of boiling alcohol. The sparingly soluble residue was crystallised from acetic acid, in which it is sparingly soluble, and separated in orange-red needles (yield, 1 g.), m. p. 275° (Found: C, 39·2; H, 3·7; Br, 40·1%).

The constitution of this acid has not yet been definitely settled, but its properties suggest that it is an aminoazo-derivative. Heated above its melting point, it sublimes in fine red needles. It is feebly basic, forming a colourless hydrochloride, whilst on boiling with acetic anhydride it yields an acetyl derivative, which crystallises from alcohol in yellow needles, m. p. 220°.

Its potassium salt dissolves in alcohol easily, and in water sparingly, forming deep red solutions. A small quantity boiled with zinc dust in acetic acid yielded 2 : 4-dibromoaniline.

The Action of Potash on cycloazi-2 : *4-Dichlorophenylbenztriazone.*—The action of alcoholic potash on *cycloazi*-dichlorophenylbenztriazone is precisely similar to its action on the corresponding dibromo-derivative already described, and yields dichlorodiazoaminobenzene-2′-carboxylic acid, together with another more stable and deeply coloured acid of the same composition. These acids were separated in the manner described for the dibromo-derivatives.

2 : 4-*Dichlorodiazoaminobenzene-2'-carboxylic acid*,
$C_6H_3Cl_2{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CO_2H$,
prepared from *cycloazi*-dichlorophenylbenztriazone by the action of potash and also directly from dichlorobenzenediazonium chloride and anthranilic acid, crystallises from alcohol, in which it is moderately easily soluble, in yellow needles, which melt at 163—167°, decomposing with a sudden puff (Found: Cl, 23·15; C, 50·2; H, 3·2; N, 13·2. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9; C, 50·3; H, 2·9; N, 13·5%).

On vigorous reduction with zinc in boiling acetic acid, the compound yielded 2 : 4-dichloroaniline, and anthranilic acid, m. p. 144°.

The potassium salt of this acid is almost insoluble in water, and moderately soluble in alcohol, crystallising from the latter in fine, pale yellow needles, m. p. 220° (decomp.).

The isomeric acid, $C_{13}H_9O_2N_3Cl_2$, separates from acetic acid, in which it is only sparingly soluble, in orange-red needles, m. p. 275° (Found: Cl, 23·0; N, 13·7%). In its properties it corresponds closely with the very stable, orange-red (dibromo) acid already described, m. p. 275° (see p. 332), subliming above its melting point in fine red crystals. Its potassium salt is sparingly soluble in water, but easily soluble in alcohol, giving a deep red solution.

THE QUEEN'S COLLEGE, OXFORD. [*Received, November 26th*, 1926.]

L.—*Contribution to the Physical Chemistry of Complex Salts. Part I. Transport Numbers of Copper Salicylate.*

By WILLIAM EDWARD HAMER and CHARLES R. BURY.

DURING the course of work on the derivatives of copper salicylate [$Cu(HSal)_2$, where H_2Sal = salicylic acid] it seemed desirable to determine its transport number in aqueous solution, with the object of throwing some light on its constitution, for on Werner's theory, the constitution of a complex salt is primarily an expression of its mode of ionisation.

Since hydrogen sulphide readily precipitates copper sulphide from an acid solution * of the salicylate, the latter presumably dissociates, to some extent at any rate, as a normal salt with formation of copper and salicylate ions. On the other hand, addition of alkali causes only very slow and partial precipitation of copper hydroxide; from these alkaline solutions, compounds of the type M_2CuSal_2 ($M = Na, K$, or NH_4) can be isolated (Ley and Erler, *Z. anorg. Chem.*, 1908, **56**, 404), and transport-number determinations—qualitative only, owing to the slow decomposition of the compound—show that copper is here part of the negative ion. Since salicylic acid contains the well-known chelate group, $-C(OH){=}\overset{|}{C}{-}\overset{|}{C}{=}O$, which is characteristic of a number of important complex-forming molecules (*e.g.*, acetylacetone), it is probable that the constitution of these compounds is represented by the formula

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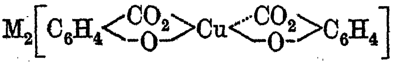
* If hydrogen sulphide is passed into a neutral solution of the compound containing no other electrolyte, a colloidal solution of copper sulphide is obtained, just as in the well-known method of preparing mercuric sulphide sols from mercuric cyanide.



$$M_2\left[C_6H_4 < \substack{CO_2\\ O} > Cu < \substack{CO_2\\ O} > C_6H_4\right]$$

(Weinland, "Komplex-verbindungen," 1919, p. 193) and that copper salicylate itself is present in solution largely as the corresponding acid, $H_2(CuSal_2)$.

Titration with alkali, the end-point being determined by means of the conductivity (since the deep colour of the solutions prohibits the use of indicators), gave sharply defined V-shaped curves indicating that the compound is a monobasic acid. The evidence is thus in favour of copper salicylate being a complex acid; the precipitation of copper sulphide by hydrogen sulphide merely proves the existence of traces of copper ions in solution.

EXPERIMENTAL.

Copper salicylate was prepared from copper sulphate and sodium salicylate, washed, recrystallised from water until free from sulphate, and air-dried. Temperatures above 60° were avoided on account of the ready decomposition.

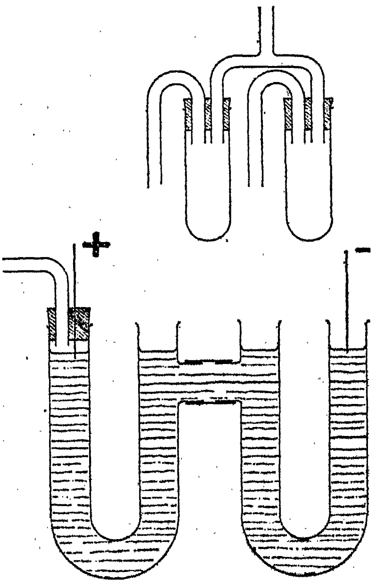
Preliminary experiments showed that the solubility of copper salicylate at 25° is 10·19 g. (0·0302 g.-mol.) per litre of solution: transport-number determinations are thus restricted to somewhat dilute solutions and the highest accuracy is unattainable.

The cell (Fig. 1), of 160 c.c. capacity, constructed throughout from tubing of the same diameter, was made in two pieces and connected by rubber tubing. It was kept in a thermostat at 25·0° ± 0·2°. A current of 10—15 milliamps. was passed between the two platinum electrodes for 1—3 hours; a precipitate (which appears to be the compound CuSal, salicylic acid acting as a dibasic acid) separated at the cathode, causing a rapid increase in the resistance with consequent fall of current; to obviate this, the cathode was lowered slightly every 10 minutes, thus exposing a fresh surface to the solution. This precipitate caused a stirring of the cathode liquid and also precluded its analysis; the transport numbers are therefore based on analysis of the anode portions only.

During preliminary experiments, inconsistent results were obtained owing to leakage of electricity through the rubber joint into the bath. To eliminate, or alternatively to detect, this source of error, the joint was waxed and two copper voltameters were used, one connected to the anode and the other to the cathode.

At the end of the experiment, two centre portions—the anode centre and the cathode centre portions, each of about 20 c.c.—were withdrawn simultaneously from the two inner limbs by means of the device shown in the upper part of Fig. 1. Withdrawal of the centre portions left the anode and cathode portions isolated in the two U-tubes. The cell was then disconnected at the rubber joint, and the anode portion removed for analysis. All analyses were by weight, not volume of solution. Copper was estimated by Volhard's method (Classen, "Ausgewählte Methoden der Analytischen Chemie," 1901, I, p. 87), since the electrolytic and iodine–thiosulphate methods fail in the presence of salicylic acid.

FIG. 1.



The results are in Table I: cols. 1, 2, and 3 give, respectively, the initial concentrations and the concentrations of the anode-centre

TABLE I.

Concentrations.			Voltameter.		Anode portion.		
Initial.	Anode-centre.	Cathode-centre.	Anode (g.).	Cathode (g.).	Weight (g.).	Copper (g.).	Transport number of cation.
0·02746	0·02755	0·02672	0·0510	0·0508	55·83	0·06484	0·628
	0·02750	0·02701	0·0532	0·0528	52·56	0·05766	0·633
	0·02732	0·02707	0·0406	0·0410	52·06	0·06386	0·646
0·01823	0·01816	0·01852	0·0341	0·0341	54·89	0·04191	0·630
	0·01834	0·01849	0·0342	0·0347	58·88	0·04621	0·627
0·01399	0·01399	0·01391	0·0214	0·0216	55·03	0·03562	0·613
0·01249	0·01247	0·01241	0·0185	0·0187	53·24	0·03067	0·617
	0·01243	0·01250	0·0154	0·0154	53·10	0·03244	0·623
						Mean	0·626

and the cathode-centre portions, in mols. per 1000 g. of water; cols. 4 and 5 show the increase in weight of the cathodes of the two copper voltameters; in cols. 6 and 7 are the weights and copper contents of the anode portion removed after the experiment, and in col. 8 are the calculated values of the transport number of the cation. No change of transport number with concentration can be detected; deviations from the mean appear to be due entirely to experimental error.

Discussion.

Neither the mobility of the copper nor that of the salicylate ion is known accurately at 25°, but assuming these to be 54 and 36, respectively, the transport number of the cation of copper salicylate should be 0·60 if it ionised as a normal cupric salt; whereas, if copper salicylate were a complex acid, there should be an increase in concentration of copper at the anode. The agreement of experiment with the first hypothesis, and the fact that the transport number does not change with concentration, show that copper salicylate ionises in aqueous solution as a normal salt—an unexpected result in view of the arguments put forward in the introduction.

Further consideration shows that hydrogen-ion concentration must have a considerable effect on the stability of the complex ion, and that the indisputable evidence for copper salicylate being a complex acid applies only to alkaline solutions. Assuming the existence of the complex negative ion $(CuSal_2)''$, this must dissociate to some extent into its components :

$$2H^{\cdot} + (CuSal_2)'' \rightleftharpoons Cu^{\cdot\cdot} + 2HSal'.$$

For the conditions of equilibrium of this reaction

$$[H^{\cdot}]^2[(CuSal_2)'']/[Cu^{\cdot\cdot}][HSal']^2 = K_s$$
$$\text{or } [(CuSal_2)'']/[Cu^{\cdot\cdot}] = K_s[HSal']^2/[H^{\cdot}]^2$$

where square brackets indicate concentrations, or, more correctly, activities, which at great dilutions are approximately equal to concentrations. The quantity on the left of the second equation is a measure of the stability of the complex ion; if all the copper is present in the form of a complex ion, its value is infinite; if all is present as simple ions, its value is zero. On combining this with the relation $[HSal'][H^{\cdot}] = K_d[H_2Sal]$, where K_d represents the first ionisation constant of salicylic acid, and with the assumption of equality of positive and negative ions, one obtains the equation :

$$\frac{[(CuSal_2)'']}{[Cu^{\cdot\cdot}]} = \frac{K_sK_d^2(2x - [H^{\cdot}])^2}{[H^{\cdot}]^2(2[H^{\cdot}] + K_d)^2} = \frac{4K_sx^2}{[H^{\cdot}]^2} \text{ (approximately)}$$

where x is the total concentration of copper salicylate in solution, independently of its nature. In neutral and alkaline solution, where $[H^{\cdot}]$ is not greater than 10^{-7}, no error will be caused by using the simpler approximate expression. The stability of the complex ion depends, therefore, on the total concentration of the compound and on the hydrogen-ion concentration; it should be increased about 10^{12} fold on passing from neutral to $N/10$-alkaline solution.*

It is possible to make a rough estimate of the value of K_s, for in a solution in which the concentration of copper salicylate is $0{\cdot}02M$ and that of sodium hydroxide is $0{\cdot}1N$, copper hydroxide is only precipitated very slowly, which shows that practically all the copper is in the form of complex ion and that the solubility product of copper hydroxide is only just exceeded. Assuming a value of 2×10^{-13} for the solubility product (Immerwahr, *Z. anorg. Chem.*, 1900, **24**, 269), K_s is 6×10^{-15}; in a neutral solution of the same strength (*i.e.*, $0{\cdot}02M$) only one-thousandth of the copper should be present as complex ion. Copper salicylate must therefore undergo a complete change in constitution on passing from neutral to alkaline solution; in other words, it is a "pseudo-acid." The change in colour of its solutions from light blue to dark green, on titration with alkali, will be regarded by many as confirmation of this view.

Similar considerations as to the influence of hydrogen-ion concentration on stability must apply to all complex ions of the type (MX_n), where M is a metal and HX a weak acid, although the equation connecting these factors will depend on the particular complex ion under consideration. It is noticeable that, whilst there are numerous salts containing complex negative ions of this type, the corresponding acids are seldom known; even when they can be prepared, which is only possible with the most stable complex ions, they are unstable compounds.

According to the equation given above, the stability of the complex ion depends on the concentration of the salt; copper salicylate is too insoluble to permit of a study of its transport number over any wide range of concentrations. Preliminary experiments with the very similar, but more soluble, nickel compound, which it is hoped to publish soon, indicate that it resembles the copper compound in dilute solution, and that appreciable quantities of complex ion are present in more concentrated solutions.

It appears to be a corollary of the complete ionisation theory of

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* $[H^{\cdot}]$ cannot be varied at will without the addition of acid or alkali; if the presence of this is taken into account, solution of six simultaneous equations leads to a more complicated expression, which reduces to the same approximate form when $[H^{\cdot}]$ is small.

Milner, and of Debye and Hückel, that the terms "pseudo-acid" and "weak acid" are synonymous; it is therefore reasonable to ascribe the behaviour of copper salicylate on titration to the fact that the complex acid, $H_2(CuSal_2)$, is a weak one. With weak dibasic organic acids, the conducto-titrimetric method gives an end-point corresponding to neutralisation of the first hydrogen ion, whilst the second end-point, corresponding to complete neutralisation, is seldom obvious.

Summary.

The transport numbers of copper salicylate in aqueous solution have been determined.

Evidence is presented in favour of the view that copper salicylate is a pseudo-acid, and that, whilst in neutral solution it ionises as a normal copper salt, in alkaline solutions it is present as the salt of a complex cuprisalicylic acid.

A consideration of the ionic equilibria involved indicates that the stability of all complex ions of this type depends to a large extent on the concentration of the hydrogen ions in the solution.

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[*Received, July 3rd*, 1926.]

LI.—*The Ratio of the Heats of Combustion of Benzoic Acid and Salicylic Acid. (A Reply to P. E. Verkade and J. Coops.)*

By Endre Berner.

Recently Verkade and Coops (J., 1926, 1437), in a reply to me (J., 1925, **127**, 2747), held that their previously determined value of the heat of combustion of salicylic acid, 5241·7 cal.$_{15}$. per g. (air) (*Rec. trav. chim.*, 1924, **43**, 561), is correct, as new determinations have given the same result. They conclude from this that my value for this heat of combustion, 5237·4 cal.$_{15}$. per g. (air), is too low and that the reason for this might be an error in the heat capacity of my calorimeter. In support of the correctness of their value, they refer to the results of Roth and of Swientoslawski, who found very nearly the same value, *viz.*, 5241·3 and 5242·4, respectively. Notwithstanding this, I am obliged to consider my value of the heat of combustion of salicylic acid to be the correct one, especially as a new comparison of the heat of combustion of a fresh standard sample of benzoic acid, from the Bureau of Standards, with that of purified salicylic acid gave very nearly the same ratio of the heats of combustion of the two substances, *viz.*, 1·2074 (vac.), as that found previously [1·2073 (vac.)]. In this comparison, as will be seen below, the heat capacity of the calorimeter was not introduced at all into the calculation of the result, the ratio being calculated directly from the rise in temperature when the two substances were burned.

In my previous paper, I was of the opinion that the difference between my value and that of Verkade and Coops was due to insufficient purity of the samples used by these authors, because we found about the same value for Merck's salicylic acid ("für kalorimetrische Bestimmungen"), and also because I found that this value was altered after purification of the sample. However, later investigations have shown that the sample from Merck, which I used, was an impure one. Another sample, obtained from Merck during 1926, has the same heat of combustion as my purified samples. Verkade and Coops also have burned two of my samples and found the same value as for their original samples. The discrepancy between their value and my own cannot, therefore, be due to impurity of the samples, but must be caused by a systematic error in the determinations.

Verkade and Coops submit that they have no reason to doubt the correctness of their value, because the ratios of the heats of combustion of benzoic acid and naphthalene and of benzoic acid and cane-sugar, determined by themselves, are in full agreement with those which have been obtained in careful work by other authors, and at present are generally accepted. They suggest, therefore, the possibility that in burning naphthalene and cane-sugar I may find other values for these ratios. I cannot believe this to be relevant to the present discussion, which only concerns the ratio of the heats of combustion of benzoic acid and salicylic acid. Presumably it should be easier to determine the exact ratio in the case of the chemically similar substances benzoic acid and salicylic acid than in the case of benzoic acid and the chemically different substances naphthalene and cane-sugar. As is well known, naphthalene has a relatively high vapour pressure and therefore evaporates appreciably even at the ordinary temperature. Cane-sugar, which is completely purified only with difficulty, generally needs auxiliary substances for ignition, and even then incomplete combustion is often the result. As a matter of course, these facts make the heats of combustion of naphthalene and cane-sugar less trustworthy than those of benzoic and salicylic acids, which are not volatile and do not need auxiliary substances for ignition.

EXPERIMENTAL.

The ratio of the heats of combustion of benzoic and salicylic acids has now been redetermined as follows.

A series of 22 combustions was carried out, under exactly the same conditions, with benzoic acid and salicylic acid alternately, *i.e.*, 11 combustions with each. The quantities of the substances used, about 0·64 and 0·78 g., respectively, always caused an equal rise, of about 1°, in the temperature of the calorimeter, the mean temperature being 19°. An oxygen pressure of 35 atm. was used, as this sufficed for the complete combustion of both substances. The ignition was effected electrically by means of a very thin platinum wire and without the aid of auxiliary substances. A detailed description of the calorimeter and method has recently been published in another journal (*Archiv for Mathematik og Naturvidenskab, Oslo,* 1926, **39**, Nr. 6).

The preparations used in the present investigation are: A standard sample of benzoic acid (39*c*) from the Bureau of Standards, Washington; a sample of benzoic acid (590) purified in the same way as sample 517 in my previous paper; three samples of salicylic acid, 571 II*b*, 572 III, and 572 IV, which were also used in my first investigation; and a sample of salicylic acid "von Heyden," purified by Verkade by crystallising it twice from water and once from chloroform (designated "Verk.").

After the necessary corrections had been applied for loss of heat and for formation of nitric acid, the rise in temperature of the calorimeter was calculated on the basis of 1 g. of the substance (weighed in a vacuum) being burned. The following are the results of the 22 combustions.

Benzoic Acid.		*Salicylic Acid.*	
Sample.	Rise in temp. for 1 g. of subst. (vac.).	Sample.	Rise in temp. for 1 g. of subst. (vac.).
39*c*	1·5549°, 1·5549°,	571 II*b*	1·2883°, 1·2879°.
„	1·5551 , 1·5550 ,	572 III	1·2878 , 1·2878 .
„	1·5550 , 1·5550 ,	572 IV	1·2883 , 1·2878 .
„	1·5554 , 1·5548 ,	Verk.	1·2876 , 1·2879 ,
„	1·5550 .	„	1·2879 , 1·2880 ,
590	1·5550 1·5555 .	„	1·2878 .
Mean	1·55505	Mean	1·28792

The ratio of the heats of combustion of benzoic acid and salicylic acid is accordingly $1{\cdot}55505/1{\cdot}28792 = 1{\cdot}2074_1$ (vac.). Previously $1{\cdot}2073_4$ (vac.) was found. The mean of the two determinations is $1{\cdot}2073_7$ (vac.). As the heat of combustion of benzoic acid is fixed at 6319 cal._{15}. per g. (vac.), the heat of combustion of salicylic acid is 5233·7 cal._{15}. per g. (vac.), or 5237·3 per g. (air).

The possible errors arising in this determination will be considered briefly. The accuracy of the measurement of the heat evolved during combustion is dependent only on the accuracy of the determination of the rise in temperature, as the heat capacity of the calorimeter was always the same. Thus the same quantity of water and the same pressure of oxygen were used, and, further, the difference between the heat capacities of the products of combustion and that of the oxygen necessary for the combustion is very nearly the same in the case of the quantities used of the two substances. By means of a trustworthy platinum resistance thermometer the temperature could be read accurately to 0·0001° or less. The correction for loss of heat generally amounted to about 0·2% of the total heat evolved. Even an error of 10% in the calculation of this correction would, therefore, result in an error of only 2 parts per 10,000 in the final result. The heat of formation of nitric acid varied from 0·4 to 0·6 cal. The total corrections in my experiments amounted, accordingly, to only 2—2·5 parts per 1000.

Another cause of error is to be found in the combustion process in the bomb. Here, an error might arise either from incomplete combustion of the substance or from the contamination of the oxygen by combustible impurities. In my experiments, the combustion of the substance was complete, as no soot could be detected in the bomb and no carbon monoxide could be found in the products of combustion. Even very small quantities of carbon monoxide can be detected when about 2 litres of the gaseous products of combustion are collected in a bottle and shaken thoroughly with 15 c.c. of a dilute solution of palladium chloride. I have previously shown that oxygen, prepared from liquid air, often contains small quantities of combustible impurities (see the detailed description), and that special attention should always be paid to the oxygen used in calorimetric work. The oxygen used in the present case was free from such impurities, as ensured by passing it, before it was filled into the bomb, through a heated, thick-walled copper tube filled with palladium asbestos and pieces of platinum.

In conformity with what has been said above, I must abide by the correctness of my value of the ratio of the heats of combustion of benzoic acid and salicylic acid, *viz.*, 1·2074 (vac.).

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[*Received, November 26th,* 1926.]

LII.—*The Isomerism of Reduced Derivatives of Quinoxaline. Part II. The Stereoisomeric* 2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalines.*

By Charles Stanley Gibson.

Like 2 : 3-diphenylquinoxaline (J., 1923, **123**, 1570), 2 : 3-dimethylquinoxaline (Gabriel and Sonn, *Ber.*, 1907, **40**, 4852), on reduction with sodium and ethyl alcohol, yields a mixture of two 2 : 3-disubstituted 1 : 2 : 3 : 4-tetrahydroquinoxalines, $C_6H_4<\begin{matrix}NH\cdot CHMe\\ |\\ NH\cdot CHMe\end{matrix}$. These two bases may be separated by taking advantage of the fact that the oxalate and the picrate of the externally compensated base are both less soluble than the corresponding salts of the *meso*-base.

The *meso*-base has been examined and characterised by the preparation of a number of simple derivatives. The externally compensated base has been resolved by means of *d*- and *l*-tartaric acids, which have, in this case, proved more useful than the stronger acids derived from optically active camphor. Whilst enantiomorphism in the crystalline form of the optically active bases has again been demonstrated, the analogy to the stereoisomerism of the tartaric acids is not so complete in this case as in the former, since the externally compensated base now described is probably a pseudo-racemic mixture, the melting points of all mixtures of the two optically active bases being between the melting point of the optically active bases and that of the externally compensated base. The rotatory powers of the bases are markedly higher than those of the corresponding 2 : 3-diphenyl derivatives previously described and the acyl derivatives possess considerable rotatory powers opposite in sign to those of the optically active bases from which they are prepared.

The following is a summary of the constants of the more important compounds now described :

	M. p.	$[M]^{20°}_{5461}$.
l-2 : 3-Dimethyltetrahydroquinoxaline	94·5°	−181·4°
d-2 : 3-Dimethyltetrahydroquinoxaline	94·5	+181·9
dl-2 : 3-Dimethyltetrahydroquinoxaline	101—102	—
meso-2 : 3-Dimethyltetrahydroquinoxaline	111—112	—
1-Benzoyl derivative of *l*-base	233—234	+983·3
1-Benzoyl derivative of *d*-base	233—234	−981·7
1-*p*-Toluenesulphonyl derivative of *l*-base	172—173	+211·3

Experimental.

meso-2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*.

2 : 3-Dimethylquinoxaline was prepared in considerable quantities from diacetyl and *o*-phenylenediamine as described by Gabriel and

Sonn (*loc. cit.*). It was purified by steam distillation, and crystallised from the hot distillate in long, prismatic needles which probably contain three molecules of water of crystallisation (Found: H_2O, 24·6. $C_{10}H_{10}N_2,3H_2O$ requires H_2O, 25·5%). The anhydrous compound melts at 104·5—105·5° (compare Gabriel and Sonn).

The most satisfactory method of reducing the above base is by means of sodium in boiling absolute ethyl-alcoholic solution. The base (10 g.) was dissolved in boiling ethyl alcohol (300 c.c.) and sodium (25 g.) introduced in small lumps, a further small quantity of alcohol being used if necessary to facilitate the solution of the last portions of sodium. The alcoholic solution from two experiments was allowed to cool and acidified with concentrated hydrochloric acid (170 c.c.), the sodium chloride filtered off, and the filtrate and washings were evaporated to dryness. The residue was dissolved in dilute hydrochloric acid and the reduced mixed bases were precipitated by means of excess of sodium hydroxide, filtered off, washed with water, and dried in a vacuum desiccator; a further small quantity of the mixed bases was obtained by extraction of the alkaline solutions with ether (total yield, 175 g. from 190 g. of 2 : 3-dimethylquinoxaline).

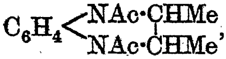
In the earlier experiments, it had been proved that when equivalent quantities of the reduced mixed bases and picric acid were mixed in alcoholic solution, the picrate of what was subsequently shown to be *dl*-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline was very much less soluble than that of the *meso*-base. Under certain conditions, however, which were not fully investigated, the base liberated from the less soluble picrate was contaminated with a deep red base, indicating that oxidation had taken place. Subsequently it was found possible to separate the two bases in a state of greater purity and more easily by means of oxalic acid, the oxalate of the externally compensated base being again the less soluble in ethyl alcohol.

12·4 G. (1 mol.) of the mixed bases dissolved in boiling ethyl alcohol (120 c.c.) were mixed with 9·7 g. (1 mol.) of crystalline oxalic acid dissolved in 40 c.c. of hot alcohol. The crystalline oxalate (p. 346) which separated was filtered off when the solution had stood for some hours. The alcoholic filtrate was evaporated to dryness, the residue suspended in water, basified with ammonia, and the base extracted thoroughly with benzene. The base obtained on evaporation of the benzene solution was repeatedly crystallised from benzene–ligroin and finally from alcohol until its melting point was no longer altered. It was obtained in almost colourless plates, m. p. 111—112°. Under these conditions, this internally compensated base forms approximately 75% of the reduction product of 2 : 3-dimethylquinoxaline (Found : C, 73·9; H, 8·9. $C_{10}H_{14}N_2$ requires C, 74·0; H, 8·7%).

meso-2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was examined crystallographically by Dr. G. M. Bennett of the University of Sheffield, to whom I am very greatly indebted for the crystallographic reports in the present paper. It crystallises in the monoclinic system with $a : b : c = ? : 1 : 0·625$; $\beta = 91°\ 5'$. Large, flat, rhomb-shaped crystals were obtained from acetone, developed on $a(100)$ and bounded by the form $m(011)$, but they were somewhat irregular and the angular values are only approximate :

	$a(100)$.	$m(011)$.	$m'(01\bar{1})$.
ϕ	0° 0′	*88° 16′	*268° 16′
ρ	90° 0′	*32° 2′	32° 2′

There is a perfect cleavage in the plane $a(100)$. The extinction on a is along the diagonal, which confirms the position of the plane of symmetry, and the crystals are biaxial.

meso-1 : 4-*Diacetyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*,  $C_6H_4<\begin{matrix}NAc\cdot CHMe\\ |\\ NAc\cdot CHMe\end{matrix}$, was prepared by heating the base with an excess of acetic anhydride on the water-bath for 1 hour. It crystallises from hot water in long, colourless needles, m. p. 145—146° (Found : C, 68·2; H, 7·3. $C_{14}H_{18}O_2N_2$ requires C, 68·25; H, 7·4%).

meso - 1 : 4-*Dibenzoyl* - 2 : 3-*dimethyl* - 1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by the Schotten-Baumann method, using a considerable excess of benzoyl chloride. It crystallises from ethyl alcohol in thin, colourless prisms, m. p. 218·5—219·5° (Found : C, 77·4; H, 6·4; N, 7·6. $C_{24}H_{22}O_2N_2$ requires C, 77·8; H, 6·0; N, 7·6%).

The following compounds were obtained by treating the base with the acyl chloride in pyridine and isolating the product in the usual manner.

meso-1-*Benzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* is much more soluble in alcohol than the dibenzoyl derivative, a small quantity of which is always obtained at the same time. It crystallises from alcohol in colourless, massive prisms, m. p. 137—138° (Found : C, 77·0; H, 6·9; N, 11·1. $C_{17}H_{18}ON_2$ requires C, 76·6; H, 6·8; N, 10·5%). It yields a colourless hydrochloride sparingly soluble in water and an almost colourless nitroso-compound which begins to decompose without melting at about 140°.

meso-1 : 4-*Di*-m-*nitrobenzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* crystallises from chloroform–ethyl alcohol in very pale yellow needles, m. p. 243—244° (Found : C, 62·6; H, 4·5. $C_{24}H_{20}O_6N_4$ requires C, 62·6; H, 4·4%).

meso-1-p-*Nitrobenzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinox-*

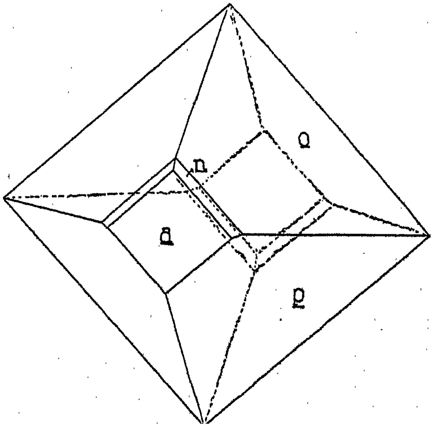
aline crystallises from ethyl alcohol in red needles, m. p. 167° (Found: C, 65·55; H, 5·55. $C_{17}H_{17}O_3N_3$ requires C, 65·5; H, 5·5%).

meso-1-p-*Toluenesulphonyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* crystallises from ethyl alcohol in colourless prisms, m. p. 183—184° (Found: C, 64·55; H, 6·3. $C_{17}H_{20}O_2N_2S$ requires C, 64·5; H, 6·4%).

meso-1 : 4-*Diphenylcarbamyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by keeping the base and an excess of phenylcarbimide in purified and dry acetone solution for some 12 hours. The product was repeatedly crystallised from purified acetone and obtained in colourless, soft needles, m. p. 190—191° (Found: C, 71·9; H, 5·9; N, 14·2. $C_{24}H_{24}O_2N_4$ requires C, 72·0; H, 6·0; N, 14·0%).

meso-1-*Carbamyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by adding potassium cyanate (2 g.) gradually to a warm solution of the base (2 g.) in the calculated quantity of *N*/2-hydrochloric acid. The crystalline precipitate which separated in almost theoretical quantity was dried and recrystallised from benzene. Well-developed crystals were obtained, m. p. 162—163° (Found: C, 64·6; H, 7·25; N, 20·5. $C_{11}H_{15}ON_3$ requires C, 64·4; H, 7·4; N, 20·5%). Dr. Bennett's crystallographic report is:

FIG. 1.



This substance crystallises in the holohedral class of the monoclinic system with $a : b : c = 0{\cdot}9131 : 1 : 0{\cdot}9429$; $\beta = 92° 16'$. It is thus pseudo-cubic and the habit of the crystals from benzene solution is octahedral, the forms developed being *a*(100), *n*(311), *o*(111), *p*($\bar{1}11$), *o*′($1\bar{1}1$) as shown in Fig. 1. The following mean angular values were obtained from three selected crystals:

	a(100).	*n*(311).	*o*(111).	*p*($\bar{1}11$).	*o*′($1\bar{1}1$).	*p*($1\bar{1}\bar{1}$).
ϕ	0° 0′	21° 38′	*52° 2′	126° 40′	* 4° 20′	354° 58′
ρ	90° 0′	90° 0′	90° 0′	90° 0′	*38° 7′	36° 42′

No marked cleavage was observed. Optical examination confirms the fact that the crystals are biaxial. The extinction on the face *a* coincides with the diagonal of the face and an optic bisectrix emerges perpendicular to *a*.

Resolution of Externally Compensated 2 : 3-*Dimethyltetrahydroquinoxaline into its Optically Active Components.*

The crystalline oxalate * (p. 343) was suspended in water and treated with an excess of a solution of ammonia. Thorough extraction with benzene then removed a base, which was recrystallised from ligroin (b. p. 40—60°) until its melting point was unchanged. The almost colourless crystals had m. p. 101—102°, and the melting points of mixtures of this and the *meso*-base were always below 100°.

That the base having m. p. 101—102° is the externally compensated base, *dl*-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline, was proved in a preliminary experiment by resolving 2 g. of the base by means of an equimolecular quantity of *d*-α-bromocamphor-π-sulphonic acid in aqueous solution, ethyl alcohol being added in small quantities to prevent the too rapid crystallisation of any salt at the ordinary temperature. After some hours, a salt (*d*A,*l*B) was obtained and from this, without further purification, the base was liberated. This base, after one crystallisation from ligroin (b. p. 40—60°), had $[\alpha]_{5461} = -84{\cdot}5°$ in 0·5% ethyl-alcoholic solution; the base liberated from the mother-liquor from the above salt had $[\alpha]_{5461} = +45{\cdot}3°$ under similar conditions. Whilst this experiment served to prove that the base having m. p. 101—102° is the externally compensated base, the resolution could not be repeated. No fewer than twelve experiments were performed in which every effort was made to maintain the conditions of the successful experiment, but in all cases the crystalline salt yielded a base which was optically inactive. With *d*-camphor-β-sulphonic acid under analogous conditions, positive indications of the partial resolution of this base were repeatedly obtained, but the rotatory power of the base from the repeatedly recrystallised, less soluble salt was very much smaller than that observed in the first successful experiment. Similarly, attempts to resolve the base by means of *d*-α-bromocamphor-β-sulphonic acid, *d*-benzoylalanine and *d*-hydroxymethylenecamphor were tried without success.

The resolution of the base by means of *d*- and *l*-tartaric acids was immediately successful. The following describes a typical experiment. *d*-Tartaric acid (20·0 g.; 1 mol.) was dissolved in boiling water (350 c.c.), and the base (21·4 g.; 1 mol.) dissolved in the boiling solution, which was then left to cool in the ice-chest for some, hours. The salt (16·9 g.; 80% of the theoretical quantity) crystallised in long, colourless needles and yielded a base which in a 0·6% ethyl-alcoholic solution had $[\alpha]_{5461} = -90{\cdot}4°$. The crystalline salt was therefore the *d*A,*l*B salt. The crude base (13·0 g.) obtained from the mother-liquor was treated with an equivalent quantity (12·0 g.) of *l*-tartaric acid (obtained by resolving racemic acid in the manner described by Marckwald, *Ber.*, 1896, **29**, 42) under exactly similar conditions to the above. The salt (15·5 g.), *l*A,*d*B, was similar in properties to the salt previously obtained, and yielded a base which in 0·6% ethyl-alcoholic solution had $[\alpha]_{5461} = +97{\cdot}2°$. The base recovered from the mother-liquor from the *l*A,*d*B salt amounted to 4·85 g., so that practically the whole of the base originally taken was accounted for.

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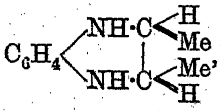
* In the first experiments the *dl*-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline was liberated from the less soluble picrate. The base so obtained was identical in all respects with that obtained from the less soluble oxalate.

In order to obtain the optically pure *l*-base, the various specimens of recrystallised *l*-base whose rotatory powers in ethyl alcohol varied from $[\alpha]_{5461} = -96{\cdot}2°$ to $-90{\cdot}4°$ were mixed and added gradually to rather more than the equivalent quantity of pure *d*-tartaric acid, dissolved in sufficient boiling water, so that the whole remained dissolved at the boiling point. This solution was rapidly filtered and the filtrate left to crystallise. Pure l-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* d-*tartrate*, $C_{10}H_{14}N_2,C_4H_6O_6,2H_2O$, separated, on cooling, in characteristic, long, colourless needles which were separated in the usual manner. The anhydrous salt begins to decompose at about 149° (Found: H_2O, 10·5. $C_{14}H_{20}O_6N_2,2H_2O$ requires H_2O, 10·4%. Found in anhydrous material: C, 54·0; H, 6·7. $C_{14}H_{20}O_6N_2$ requires C, 53·8; H, 6·5%). The salt cannot be conveniently recrystallised, as its solutions darken somewhat rapidly. Its rotatory power was determined in ethyl-alcoholic solution at 20°: $c = 1{\cdot}03$, $l = 4$, $\alpha_{5461} = -2{\cdot}07°$, $[\alpha]_{5461} = -50{\cdot}2°$.

Pure d-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* l-*tartrate* was obtained in a similar manner from the recrystallised specimens of the not quite completely resolved *d*-base and pure *l*-tartaric acid. It had analogous properties (Found in anhydrous material: C, 54·1; H, 6·8. $C_{14}H_{20}O_6N_2$ requires C, 53·8; H, 6·5%). Its rotatory power was determined in ethyl-alcoholic solution at 20°: $c = 1{\cdot}004$, $l = 4$, $\alpha_{5461} = +2{\cdot}00°$, $[\alpha]_{5461} = +49{\cdot}9°$.

l- *and* d-2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalines*,

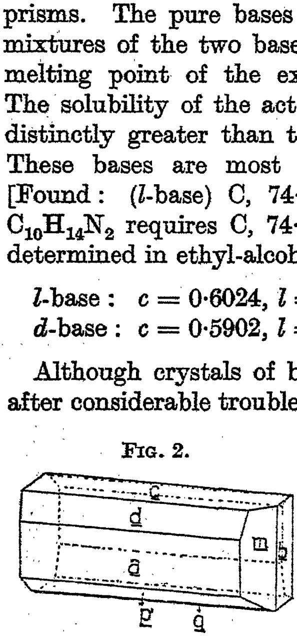


were obtained in each case from the corresponding pure tartrate. The salt was suspended in water, a slight excess of ammonia added, and the mixture extracted thoroughly with benzene. The benzene solution after washing and drying was evaporated to dryness, and the residue extracted carefully with redistilled ligroin (b. p. 40—60°) in a Soxhlet apparatus. The pure base was obtained in massive, but distorted, almost colourless prisms. The pure bases have m. p. 94·5° and melting points of mixtures of the two bases lie between this melting point and the melting point of the externally compensated base (101—102°). The solubility of the active bases in organic solvents is high and distinctly greater than that of the externally compensated base. These bases are most conveniently recrystallised from ligroin [Found: (*l*-base) C, 74·1; H, 8·8; (*d*-base) C, 74·0; H, 9·1. $C_{10}H_{14}N_2$ requires C, 74·0; H, 8·7%]. The rotatory powers were determined in ethyl-alcoholic solution at 20°:

l-base: $c = 0{\cdot}6024,\ l = 4,\ \alpha_{5461} = -2{\cdot}70°,\ [\alpha]_{5461} = -112{\cdot}0°.$
d-base: $c = 0{\cdot}5902,\ l = 4,\ \alpha_{5461} = +2{\cdot}65°,\ [\alpha]_{5461} = +112{\cdot}3°.$

Although crystals of both the *l*- and the *d*-base were obtained after considerable trouble by the slow evaporation of their solutions in pure acetone, only those of the *d*-base, examined by Dr. Bennett, need be described.

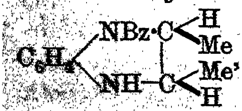
FIG. 2.



d-2 : 3-Dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline crystallises in the sphenoidal class of the monoclinic system with $a : b : c = 1{\cdot}362 : 1 : 0{\cdot}892$; $\beta = 91°\ 56'$. The forms observed were *a*(100), *c*(001), *b*(010), *m*(110), *p*($\bar{1}$01), *q*($\bar{3}$05), *d*(601). Some crystals are simple combinations of *m* and *c*, but others show the definitely enantiomorphous habit depicted in Fig. 2, with elongation along the *b* axis. Owing to the imperfections of the crystals some of the following mean angular values (obtained from five crystals) are a little uncertain:

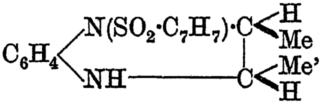
	a(100)	*d*(601)	*c*(001)	*q*($\bar{3}$05)	*p*($\bar{1}$01)	*m*(110)	*b*(010)
φ ...	0° 0′	13° 47′	*88° 4′	109° 15′	*121° 54′	0° 0′	0° 0′
ρ ...	90° 0′	90° 0′	90° 0′	90° 0′	90° 0′	*36° 18′	−0° 6′

There is no marked cleavage. The substance is biaxial. The extinction appears to be straight on *a* and *c*, and the optic axial plane coincides with *b*.



l-1-*Benzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, was prepared by treating a solution of the *l*-base (1·5 g.) with a benzene solution of benzoyl chloride (3 g.) and sodium hydroxide in the usual manner at the ordinary temperature. The product was recrystallised three times from benzene, its m. p., 233—234° (decomp.), not altering after the first crystallisation. It was obtained in small, colourless needles (Found: N, 10·5. $C_{17}H_{18}ON_2$ requires N, 10·5%). Its rotatory power was determined at 20° in ethyl alcohol, in which solvent the substance is only sparingly soluble: $c = 0{\cdot}2338$, $l = 4$, $\alpha_{5461} = +3{\cdot}46°$, $[\alpha]_{5461} = +369{\cdot}7°$.

d-1-*Benzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 233—234° (decomp.), was obtained in a precisely similar way from the *d*-base, and the compound has analogous properties (Found: C, 76·4; H, 6·7; N, 10·4. $C_{17}H_{18}ON_2$ requires C, 76·6; H, 6·8; N, 10·5%). Its rotatory power was determined in ethyl-alcoholic solution at 20°: $c = 0{\cdot}3596$, $l = 4$, $\alpha_{5461} = -5{\cdot}31°$, $[\alpha]_{5461} = -369{\cdot}1°$.

l-1-p-*Toluenesulphonyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*,  $C_6H_4\left\langle\begin{array}{l}N(SO_2{\cdot}C_7H_7){\cdot}C\left\langle\begin{array}{l}H\\Me\end{array}\right.\\ NH\text{————}C\left\langle\begin{array}{l}Me\\H\end{array}\right.\end{array}\right.$, was prepared from the *l*-base (1·5 g.) and *p*-toluenesulphonyl chloride (3·7 g.) in pyridine solution. The product crystallised from alcohol in small, colourless plates, m. p. 172—173° (decomp.) (Found: N, 8·6. $C_{17}H_{20}O_2N_2S$ requires N, 8·9%). Its rotatory power was determined in ethyl alcohol at 20°: $c = 0{\cdot}5762$, $l = 4$, $\alpha_{5461} = +1{\cdot}54°$, $[\alpha]_{5461} = +66{\cdot}9°$.

I wish to express my thanks to the Government Grant Committee of the Royal Society for a grant which has covered the cost of the materials used in this investigation and to the workers in my laboratory who have made it possible for me to complete this part of the investigation.

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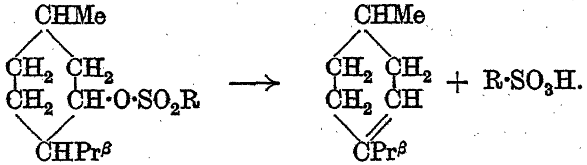
[*Received, December 13th,* 1926.]

LIII.—*The Decomposition Products of Menthyl Esters of Sulphonic Acids.*

By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE.

WHILE engaged in an examination of the optical rotation of menthyl benzenesulphonate and menthyl naphthalene-β-sulphonate, Patterson and Frew (J., 1906, 89, 332) noticed that these compounds decompose at temperatures just above their melting points, both in the homogeneous state and in nitrobenzene solution, whereas many other menthyl esters are much more stable, and are distillable at considerably higher temperatures. We have recently investigated this decomposition more fully and have found that, on direct distillation of menthyl benzene- and naphthalene-α- and -β-sulphonates under reduced pressure, the main reaction is decomposition into menthene and the corresponding sulphonic acid according to the equation



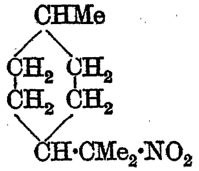
But when the heating of the homogeneous ester is carried out in sealed tubes at ordinary pressure, secondary decompositions take place with formation of hexahydrocymene, carbonaceous matter, and tarry products, whilst the menthene which is possibly first formed polymerises to dimenthene and a more complex gelatinous substance. None of the menthene appears to survive, if indeed it is formed at all.

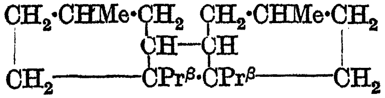
EXPERIMENTAL.

Menthyl benzenesulphonate (m. p. 80°) was prepared as described in the paper quoted above, and was then decomposed in various ways.

I. On heating the ester at 85—90° for 6 hours in a tube, which, although no pressure developed, was sealed, complete separation into two layers took place. On cooling, the lower brown layer solidified to form a low-melting, deliquescent solid. The upper layer in the crude condition had a slight positive rotation; it was separated, by distillation at 4 mm. pressure, into two fractions of b. p. 72—75° and 150—240°. The lower-boiling fraction (A) was a clear, colourless, optically-inactive liquid, distilling at ordinary pressure from 167—169° (Found: C, 85·7, 85·6; H, 14·4, 14·4; *M*, cryoscopic in benzene, 142. $d_{4^\circ}^{17^\circ}$ 0·7962, n_D 1·44009; whence $[R_L]_D = 46{\cdot}35$. $C_{10}H_{20}$ requires C, 85·7; H, 14·3%; *M*, 140). The substance appears thus to be a saturated ring compound. With nitric acid (*d* 1·075), a yellow nitro-derivative was obtained, b. p. 135—137°/25 mm., n_D 1·46241, presumably therefore tertiary nitromenthane (I). The original liquid thus appears to be hexahydrocymene, which has been shown to form a tertiary nitro-compound corresponding to that which we obtained (Konowalov, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 237).

(I.)





(II.)

The higher-boiling fraction was separated by distillation under reduced pressure into a viscous, oily liquid (B), b. p. 174°/4 mm., and a gelatinous mass (C), b. p. 240—270°/4 mm. The fraction (B) (Found: C, 86·8, 86·8; H, 13·2, 13·15; *M*, cryoscopic in benzene, 273·1. $d_4^{17°}$ 0·8845, n_D 1·48704; whence $[R_L]_D = 88·14$. $C_{20}H_{36}$ requires C, 86·9; H, 13·1%; *M*, 276; $[R_L]_D$, 87·96) had a slight dextrorotation, $[\alpha]_{5461}^{17°}$ ($c = 5$ in benzene) $= +2·29°$, and did not decolorise potassium permanganate solution on standing; on treatment with bromine, hydrogen bromide was evolved. This compound closely approximates to that obtained by Tolloczko (*J. Russ. Phys. Chem. Soc.*, 1897, **29**, 39; *Chem. Zentr.*, 1898, I, 105) by treating menthol with sulphuric acid (except that his product was completely inactive), and thus appears to be dimenthene (II) (Kanonnikov, *Chem. Zentr.*, 1899, II, 860). A gelatinous compound corresponding to that (C) obtained by us was also observed by Tolloczko. Owing to the difficulty of purifying this compound, we have been unable to identify it.

Solid product. The solid substance constituting the lower layer after the heating of menthyl benzenesulphonate was deliquescent and of low melting point. We were unable to crystallise it from any solvent. It was easily soluble in water and the solution gave a strongly acid reaction. The barium salt prepared from the aqueous solution after boiling with animal charcoal was purified by recrystallisation from water [Found: H_2O, 3·9, 3·9; Ba, 29·0, 29·0. Calc. for $Ba(SO_3·C_6H_5)_2,H_2O$: H_2O, 3·8; Ba, 29·3%]. The solid substance which separates on heating menthyl benzenesulphonate is therefore mainly, or exclusively, benzenesulphonic acid.

II. *Decomposition by Direct Distillation.*—If, instead of being heated in a sealed tube, menthyl benzenesulphonate be directly distilled at a pressure of 4 mm., a vapour condensing to a colourless liquid passes over at 68° (the substance, heated in an oil-bath, being meanwhile at a temperature a little above its melting point), and a brown, deliquescent solid remains in the flask.

The liquid (D) boiled at 165° under ordinary pressure and had the rotation $[\alpha]_{5461}^{20°} = +9·56°$ (Found: C, 86·8, 86·8; H, 13·15, 13·2; *M*, cryoscopic in benzene, 138·4. $C_{10}H_{18}$ requires C, 86·9; H, 13·1%; *M*, 138. $d_4^{17°}$ 0·8130, n_D 1·45162; whence $[R_L]_D = 45·72$. Calc. for $C_{10}H_{18}$ + one ethylene linking, 45·71). It formed a nitrosochloride, m. p. 117°, and thus appears to be the same menthene as obtained by Zelikov (*Ber.*, 1904, **37**, 1374) by the action of various dibasic acids such as succinic acid, tartaric acid, citric acid, phthalic acid, terephthalic acid on menthol at high temperatures, and by Tschugaev (*Ber.*, 1899, **32**, 3332) by distilling menthyl xanthates in a vacuum. The rotation of the menthene formed in such experiments varies greatly; that obtained by Tschugaev had the high rotation $[\alpha]_D = 114{\cdot}77°$, 116·06°, which may have been due to the fact that his menthyl xanthate had a fairly low melting point, 39°.

In our experiment the higher-boiling dimenthene does not appear to be formed, whilst the other product of decomposition was found, from analysis of its barium salt, to be benzenesulphonic acid.

III. *Decomposition in Solution.*—Patterson and Frew (*loc. cit.*) had already noticed that menthyl benzenesulphonate also decomposed on heating in nitrobenzene solution. We ascertained that, when it is heated in benzene solution under reflux, little decomposition takes place, whereas in toluene decomposition appears to be complete. A brown solid separated which proved to be benzenesulphonic acid; the toluene solution acquired a positive rotation, and, after distillation of the solvent, a fraction was obtained, b. p. 190°/20 mm., presumably dimenthene. No lower-boiling decomposition product appeared to be formed.

I. *Menthyl naphthalene-β-sulphonate* (m. p. 114·5°), which had been examined by Patterson and Frew, was prepared again and heated in a sealed tube at 120°. Decomposition took place, and, as in the case of the benzenesulphonate, three distillable liquids were obtained. The most easily volatile fraction (A) boiled between 167° and 169° under ordinary pressure (Found: C, 85·75, 85·6; H, 14·2, 14·4%). The liquid was inactive and was identical with the hexahydrocymene obtained from menthyl benzenesulphonate.

The middle fraction, b. p. 174°/4 mm., had a slight positive rotation (Found: C, 86·8, 86·7; H, 13·1, 13·2%). It was the same as the dimenthene, $C_{20}H_{36}$, obtained from the benzenesulphonic ester. Some of the gelatinous substance, b. p. 240—270°/4 mm., was also obtained, but was not further examined.

In this case the solid which was produced on heating crystallised with difficulty from chloroform; m. p. 80°. From it a barium salt was prepared crystallising in flat, glistening plates [Found: H_2O, 3·2, 3·2; Ba, 24·1, 24·0. Calc. for $(C_{10}H_7{\cdot}SO_3)_2Ba,H_2O$: H_2O, 3·2; Ba, 24·1%]. The decomposition product is therefore naphthalene-β-sulphonic acid.

II. When menthyl naphthalene-β-sulphonate, instead of being heated in a sealed tube, was distilled directly under 4 mm. pressure, a liquid boiling at 68° passed over and a yellow solid residue was left in the flask. The liquid boiled at 165° under ordinary pressure, had a positive rotation of $[\alpha]^{20°}_{5461} = +9·4°$, and on analysis gave values corresponding to the formula $C_{10}H_{18}$, proving it to be the menthene obtained in the corresponding experiment with menthyl benzenesulphonate. The solid was naphthalene-β-sulphonic acid, which was characterised by the analysis of its barium salt.

III. Menthyl naphthalene-β-sulphonate, heated in nitrobenzene solution at 100° or in xylene solution at 120°, decomposed and, on cooling, naphthalene-β-sulphonic acid separated. The reaction products were not further examined.

I. *Menthyl naphthalene-α-sulphonate* (m. p. 116·5°, decomp.) was prepared in 60% yield in the same way as the other two sulphonic esters, and was crystallised from alcohol. It is soluble in most common solvents and has $[\alpha]^{17·5°}_{5461}$ (in benzene; $c = 1$) $= -93·25°$ and $[\alpha]^{17·5°}_{5461}$ (in alcohol; $c = 1$) $= -114·8°$.

When it was decomposed in a sealed tube at 120°, two layers were formed. The liquid, on distillation and analysis, yielded the same three fractions as before, namely, hexahydrocymene (b. p. 167—169°/ordinary pressure. Found: C, 85·6; H, 14·4%); dimenthene (b. p. 174°/4 mm. Found: C, 86·6; H, 13·1%), and a gelatinous mass boiling from 240—270°/4 mm. The lower layer consisted of naphthalene-α-sulphonic acid, as was proved by the analysis of its barium salt [Found: Ba, 24·2, 24·1. Calc. for $(C_{10}H_7·SO_3)_2Ba,H_2O$: Ba, 24·1%].

II. On decomposition of this ester by direct distillation in a vacuum, menthene and naphthalene-α-sulphonic acid were the only products obtained and were characterised as before.

III. The ester also decomposed when heated in solution in much the same way as in the other two cases.

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[*Received, December 23rd, 1926.*]

LIV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXIV.* Menthyl Benzenesulphonate, Menthyl Naphthalene-α-sulphonate, and Menthyl Naphthalene-β-sulphonate in Various Solvents.*

By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE.

WE have examined the rotations of the esters described in the foregoing paper for three different colours of light, mercury yellow (λ = 5790), mercury green (λ = 5461), mercury violet (λ = 4358), and in several solvents which, for convenience of reference, are indicated by letters of the alphabet, namely, (*a*) ethyl alcohol; (*b*) benzene; (*c*) pyridine; (*d*) nitrobenzene; (*e*) ethylene dibromide; (*f*) quinoline. Since the object of our investigation was, in the first place, to obtain a general oversight, we examined only one solution in each case at a concentration between 4·45 and 1. The data are given in the tables of specific rotations.

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* Pt. XXIII, J., 1916, **109**, 1204.

TABLE I.

Specific Rotations of Menthyl Sulphonates in Various Solvents.

t = approximately 17·5° throughout.

Menthyl benzenesulphonate.

Solvent	a	b	c	d	e	f
Concentration	4·0	4·5	4·0	4·0	4·0	3·0
y	− 74·7°	− 65·5°	− 67·9°	− 67·4°	− 72·7°	− 64·4°
g	− 84·6	− 74·0	− 76·3	− 75·9	− 82·6	− 72·8
v	−142·2	−123·2	−127·4	−127·9	−137·6	−122·8

Menthyl naphthalene-α-sulphonate.

Solvent	a	b	c	d	e	f
Concentration	1·0	1·0	1·0	3·0	1·0	3·0
y	−101·8°	− 81·4°	− 87·3°	− 92·2°	−145·2°	− 84·8°
g	−114·8	− 93·2	− 98·4	−104·6	−163·5	− 97·2
v	−194·3	−158·1	−166·0	−178·1	−276·2	−167·1

Menthyl naphthalene-β-sulphonate.

Solvent	a	b	c	d	e	f
Concentration	1·0	1·0	1·0	3·0	1·0	3·0
y	− 56·1°	− 51·9°	− 47·7°	− 43·9°	− 49·3°	− 31·2°
g	− 64·0	− 59·3	− 55·0	− 48·7	− 56·3	− 35·1
v	−108·0	−101·9	− 92·2	− 82·6	− 95·7	− 59·1

Although the rotations vary considerably in each case with change of solvent, the change is not sufficient to cause any overlapping, so that the solutions of each substance form a separate group, the rotations of menthyl naphthalene-β-sulphonate being lowest, and those for menthyl naphthalene-α-sulphonate being highest. The rotations for the benzenesulphonate solutions lie wholly between the others. It may also be noticed that the different solvents do not influence the rotations in the same way, although there is some similarity. Quinoline, which usually has a powerful influence either towards exaltation or depression, produces the lowest rotation in menthyl naphthalene-α-sulphonate and in menthyl benzenesulphonate, and the second lowest in menthyl naphthalene-β-sulphonate. Ethylene dibromide, on the other hand, which usually has a powerful influence of the opposite character to quinoline, produces the highest rotation in menthyl naphthalene-α-sulphonate, the second highest in menthyl benzenesulphonate, and the third highest in menthyl naphthalene-β-sulphonate. On the whole, therefore, this general tendency is recognisable.

These values were then plotted on a characteristic diagram and lay with good agreement along lines intersecting one another very close to the point of origin of the diagram, and in such a way, as far as can be judged when extrapolation has to be carried out through some 35° of rotation, as to indicate little or no region of anomalous rotation dispersion. The data thus present a behaviour which we think is rare and it follows that the dispersion coefficients for all these compounds calculated by the ordinary method ought to be almost the same throughout. (For a general discussion of this subject, see J., 1916, **109**, 413.) That this is the case is shown by the following table of dispersion ratios.

TABLE II.

	Menthyl benzene-sulphonate. Dispersion.		Menthyl naphthalene-α-sulphonate. Dispersion.		Menthyl naphthalene-β-sulphonate. Dispersion.	
Solvent.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_y.	Hg_y/Hg_y.
Alcohol	1·680	0·883	1·692	0·887	1·687	0·878
Benzene	1·664	0·884	1·695	0·873	1·716	0·875
Pyridine	1·669	0·890	1·686	0·887	1·676	0·859
Nitrobenzene ...	1·685	0·888	1·703	0·881	1·698	0·902
Ethylene dibromide	1·665	0·879	1·689	0·888	1·700	0·876
Quinoline	1·685	0·885	1·709	0·872	1·683	0·889

These data, we think, form an almost unique example of constancy of ordinary dispersion ratios for a series of related substances, the rotation of which, for mercury green, varies over so wide a range as −35·1° for menthyl naphthalene-β-sulphonate in pyridine, up to −163·5° for menthyl naphthalene-α-sulphonate in ethylene dibromide.

The thanks of one of us (I. M. McA.) are due to the Department of Scientific and Industrial Research for a maintenance grant which enabled the work described in this and the preceding paper to be carried out.

UNIVERSITY OF GLASGOW. [*Received, December 23rd, 1926.*]

LV.—*The Quantitative Estimation of Mixtures of Isomeric Unsaturated Compounds. Part I. A Bromine Addition Method.*

By REGINALD PATRICK LINSTEAD.

ALTHOUGH the structural conditions necessary to promote the movement of the double bond in the three-carbon system (Birch, Kon, and Norris, J., 1923, **123**, 1361, and subsequent papers by

Kon and his collaborators) have been studied, the quantitative aspect of the subject has been somewhat neglected owing to the difficulty of analysing the mixtures of isomerides obtained. Examination of the position of equilibrium in systems possessing retarded mobility (Kon and Linstead, J., 1925, **127**, 815) would, however, enable the effects of various substituent groups to be compared and the figures thus obtained would be of interest for comparison with the Thorpe-Ingold values for valency distortion and with the values for the *o*-, *p*-, and *m*-directing powers of the same groups when substituted in the benzene nucleus (compare Ingold, Shoppee, and Thorpe, J., 1926, 1477).

In the determination of the position of equilibrium in a three-carbon system,

$$\underset{\alpha\beta\text{-form}}{\mathrm{HC{-}C{=}CX}} \qquad\qquad \underset{\beta\gamma\text{-form}}{\mathrm{C{=}C{-}CHX}}$$

the isomerides present in the equilibrium mixture must first be isolated under conditions precluding further change and their proportion can then be estimated either by physical separation of the individuals, by optical measurements, or by separation through derivatives. The results so obtained are not completely trustworthy and the best methods at present available are those based upon the selective action of reagents such as dilute sulphuric acid (Fittig, *Annalen*, 1894, **283**, 47) and hypoiodous acid (Bougault, *Ann. Chim.*, 1908, **14**, 145), both of which are stated to combine with βγ-unsaturated acids but not with the αβ-isomerides.

The principle of the new method herein described is that the composition of a mixture of αβ- and βγ-isomerides can be determined by comparing its velocity of addition to halogens with the velocities for the two pure substances, and is based upon the observations of Sudborough and Thomas (J., 1910, **97**, 715, 2450) that halogens react additively much more rapidly at a βγ- than at an αβ-double bond. Notwithstanding the observations of Bougault (*loc. cit.*; *Ann. Chim.*, 1908, **15**, 296), it is doubtful whether halogens ever react completely at a βγ-double bond under conditions in which the αβ-isomeride is unchanged. It has therefore been necessary to measure the percentage reaction over a definite interval of time.

In general, the reacting substances are used in molecular quantities, the halogen being present in the form of a stable standardised solution. Other conditions, such as the nature and state of activation of the halogen, temperature, light, concentration, the nature of the solvent, and the presence of catalysts, may be varied to bring the reaction within the region of convenient experimental investigation; *e.g.*, in a given series the unsaturated acids will require conditions more favourable to addition than will the corresponding, more positive ketones. The method has so far been used to determine the compositions of various mixtures of unsaturated acids. Preliminary work has been carried out on ketones and esters and it is hoped to communicate these results shortly.

1. *Examination of the Pure Acids.*

Materials.—The acids examined were: (1) *cyclo*Hexylideneacetic acid (Wallach, *Annalen*, 1909, **365**, 261), (2) Δ^1-*cyclo*hexenylacetic acid (Kon and Speight, J., 1926, 2727; Farrow and Kon, *ibid.*, p. 2128), (3) ββ-diethylacrylic acid, (4) β-ethyl-Δ^β-pentenoic acid, and (5) β-methyl-β-ethylacrylic acid, all three prepared by Kon and Linstead's method (*loc. cit.*), and (6) β-methyl-Δ^β-pentenoic acid, which was made by boiling β-hydroxy-β-methylvaleric acid with 12½% sulphuric acid for 2½ hours and obtained, in 35% yield, almost free from its isomeride; it was purified by fractional distillation. The acids used in the analytical work had the following physical properties: (1) Plates, m. p. 90—91°, b. p. 159—160°/22 mm., from light petroleum; (2) plates, m. p. 36—38°, b. p. 152°/23 mm.; (3) b. p. 124°/13 mm., $[R_L]_D$ 36·59 (*p*-toluidide, m. p. 81°); (4) b. p. 112°/10 mm., $[R_L]_D$ 35·82 (*p*-toluidide, m. p. 94°); (5) flattened needles, m. p. 45°, b. p. 104°/13 mm., from light petroleum (*p*-toluidide, m. p. 67°); (6) b. p. 101°/14 mm., $[R_L]_D$ 31·07 (*p*-toluidide, m. p. 84°).

The halogen used was bromine, purified by the method of Sudborough and Thomas (*loc. cit.*). The solvents were carefully freed from traces of acid and were dried and fractionated twice before use.

Reaction.—The reaction was carried out under conditions differing from those of Sudborough and Thomas (*loc. cit.*) in several details (compare also Mills, J., 1883, **43**, 435). The solutions of the reagents were mixed in bulk instead of in aliquot portions. Immediately before readings were taken, quantities of 50 c.c. each were drawn into a pipette connected by a three-way tap with a low vacuum and were run, after definite intervals of time, into a solution of potassium iodide; the liberated iodine was titrated with *N*/20-thiosulphate. The other conditions observed were as follows:

Solvent. For acids (1) and (2), carbon tetrachloride; for acids (3), (4), (5), and (6), chloroform.

Concentration. 1/60 G.-mol. per litre (1/120 g.-mol. of the acid was dissolved in 250 c.c. of the inert solvent. The equivalent amount of bromine was obtained by making the necessary quantity of a freshly standardised solution of bromine up to 250 c.c.).

Temperature. 25°, controlled by a thermostat.

Lighting. All the reactions were carried out in blackened flasks.

Results.—The absorption of bromine is abnormally fast during the first 2 minutes of the reaction, but thereafter it pursues a bimolecular course and can easily be followed. As observed by previous workers, in general the readings do not give very concordant values for the velocity coefficient, $k = x/at(a - x)$, but there is no steady rise or fall indicating the occurrence of a secondary reaction.* The results are in Table I; the values of a and $a - x$ are given by the number of c.c. of thiosulphate required at the beginning and the end of a period of t hours. All the reaction velocities are derived from figures representing fractional changes and therefore are directly comparable (with the exception of those for the *cyclo*hexane acids, where a different solvent was used). The figures are thus independent of the strength of the thiosulphate solution, which was renewed and restandardised from time to time. Two of Sudborough and Thomas's results at 15°, marked * in the table, are given for comparison.

TABLE I.

Unsaturated Acids + Bromine at 25°.

Acid.	Solvent.	*k.* Minimum.	Maximum.	Mean.	No. of readings
*cyclo*Hexylideneacetic	CCl_4	$0{\cdot}65 \times 10^{-2}$	$2{\cdot}08 \times 10^{-2}$	$1{\cdot}04 \times 10^{-2}$	6
Δ^1-*cyclo*Hexenylacetic	,,	0·43	1·91	1·07	9
β-Diethylacrylic	$CHCl_3$	$1{\cdot}17 \times 10^{-3}$	$2{\cdot}28 \times 10^{-3}$	$1{\cdot}91 \times 10^{-3}$	4
β-Ethyl-Δ^β-pentenoic	,,	$0{\cdot}74 \times 10^{-2}$	$5{\cdot}67 \times 10^{-2}$	$1{\cdot}15 \times 10^{-2}$	4
β-Methyl-β-ethylacrylic ...	,,	$0{\cdot}44 \times 10^{-3}$	$3{\cdot}53 \times 10^{-3}$	$2{\cdot}08 \times 10^{-3}$	3
β-Methyl-Δ^β-pentenoic	,,	$1{\cdot}35 \times 10^{-2}$	$2{\cdot}75 \times 10^{-2}$	$2{\cdot}03 \times 10^{-2}$	6
β-Methyl-Δ^α-butenoic *...	CCl_4	$3{\cdot}1 \times 10^{-3}$	$7{\cdot}3 \times 10^{-}$		
Δ^α-Butenoic*	,,	$4{\cdot}68 \times 10^{-6}$	$6{\cdot}16 \times 10^{-6}$	—	—

Analysis of the Results.—From the structural point of view several interesting points arise from these results. In the first place, the effect of conjugation in the αβ-acids is to give a velocity coefficient 1/10—1/100 of that found for the βγ-acid. Secondly, substitution of positive groups for hydrogen leads to an increased velocity of reaction, the *cyclo*hexane ring having an exceptionally great effect. Finally, the results for the addition of bromine to ββ-diethylacrylic acid and its Δ^β-isomeride show that the latter (*p*-toluidide, m. p. 94°; amide, m. p. 114°) has the greater velocity of reaction and is therefore the βγ-acid—a result in agreement with the observations of Kon and Linstead (*loc. cit.*) on the structure of these acids.

2. *Examination of Mixtures of the Acids.*

Materials.—The investigation of mixtures of isomeric acids was carried out with mixtures obtained by the action of alkali on the pure acids under various conditions, and with artificial mixtures of known compositions prepared by mixing together the pure isomerides.

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* Hydrogen bromide is slowly liberated from the reaction product after some time, the change being facilitated by the presence of water.

The equilibration of the acids was carried out in the manner described in the following paper. With the exception of the *cyclo*hexyl acids, the resulting mixtures were distilled under reduced pressure, a fraction covering the boiling points of both isomerides being collected in each case. The absence of saturated impurity—*e.g.*, hydroxy-acids formed by the addition of water at the double bond—was proved by determinations of the total capacity of the mixtures for nascent bromine by Vaubel's method (*J. pr. Chem.*, 1893, **48**, 75) as modified by Callan and Russell Henderson (*J. Soc. Chem. Ind.*, 1922, **41**, 161T). In all the analyses made in this way, the titration figures agreed with those required for the addition of two atoms of bromine. The results are in Table II.

TABLE II.

Acids + Nascent Bromine.

Series.	*cyclo*Hexyl.							
Initial material	αβ	βγ	αβ	αβ	αβ	βγ	βγ	βγ
% Alkali used	—	—	60	50	40	60	50	40
Br added (mg.). found	87·4	86·3	81·5	73·9	46·5	42·7	39·5	53·7
Br added (mg.). calc.*	87·4	87·7	78·7	70·4	45·8	42·3	39·5	53·7

Series.	β-Ethylpentenoic.			β-Methylpentenoic.		
Initial material	αβ	βγ	αβ	αβ	βγ	αβ
% Alkali used	—	—	60	—	—	60
Br added (mg.). found	59·3	43·3	60·3	49·9	60·7	86·3
Br added (mg.). calc.*	57·9	43·3	57·2	47·5	61·4	87·7

* Calculated for the addition of two atoms of bromine per molecule.

After proof of their purity had been obtained in this way, the mixtures of acids were examined by the bromine-addition method, the reactions being carried out exactly as with the pure acids.

Analysis of Results.—The mixtures of acids gave figures for the addition of bromine intermediate between those obtained for the parent substances. The velocity coefficients for the pure acids were not sufficiently accurate to allow of their use as constants in a mathematical analysis of the subject, and the compositions of the mixtures were therefore determined empirically by comparing the addition figures for the mixtures with those for mixtures prepared from definite quantities of the pure isomerides. This was most conveniently done in the manner indicated below.

The addition curves for the β-methylpentenoic acids (Fig. 1) show that at the end of the first 2 minutes the addition is proceeding comparatively slowly. Determinations made in this region are therefore not liable to appreciable experimental error; moreover there is little danger of discrepancies arising from side reactions which may develop later, such as that due to the catalytic effect of hydrogen bromide liberated from the products of the reaction. The connexion between composition and addition is given in Table III, which shows the percentage addition of bromine in 2 minutes to various mixtures of acids of known composition.

FIG. 1.

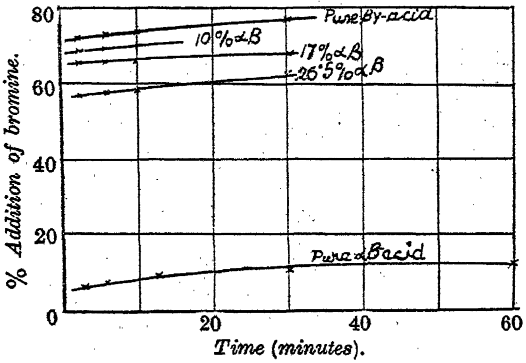


TABLE III.

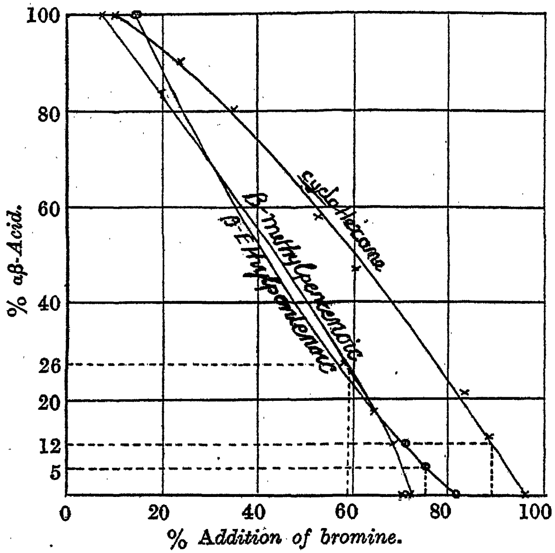
Comp. of acid. % αβ.	Comp. of acid. % βγ.	Addition. %.
*cyclo*Hexane series.		
0	100	95·6
14·3	85·7	88·1
20·9	79·3	84·0
46·0	54·0	59·9
58·0	42·0	54·3
79·7	20·3	34·7
90·1	9·9	24·0
100	0	10·4

Comp. of acid. % αβ.	Comp. of acid. % βγ.	Addition. %.
β-Ethylpentenoic series.		
0	100	81·3
5·1	94·9	74·5
8·2	91·8	70·0
100	0	15·0
β-Methylpentenoic series.		
0	100	70·2
10·1	89·9	67·9
17·0	83·0	64·2
26·5	73·5	57·6
100	0	7·2

It will be seen that the amount of addition is roughly proportional to the percentage of βγ-acid. The variation from this relationship is shown in Fig. 2, where the two-minute addition figures for the three series are plotted against composition. The complete curve has been obtained only for the *cyclo*hexane acids; in the other series, only mixtures in the neighbourhood of the equilibrium point were examined.

The compositions of the various mixtures of acids obtained on equilibration were readily determined from the addition values and reference to the appropriate curves. The positions of the equilibrium mixtures are shown by the dotted lines in Fig. 2, and the addition values and the compositions calculated from them are in Table IV.

FIG. 2.



Dotted lines represent equilibrium mixtures.

TABLE IV.

Addition Values and Compositions of Equilibrium Mixtures.

Series.	Initial acid.	% Alkali.	Time (hrs.).	% Addition of bromine (2-min.).	% αβ-Acid in mixture.
*cyclo*Hexane	αβ	60	1·0	87·9	13
	αβ	60	24·0	89·4	11
	αβ	50	1·55	87·8	13
	αβ	50	24·0	89·08	11
	αβ	40	24·0	87·8	13
	βγ	60	23·0	89·4	11
	βγ	50	24·0	87·8	13
	βγ	40	24·0	87·8	13
β-Ethylpentenoic	αβ	60	0·33	76·4	4
	αβ	60	0·33	74·1	5
	βγ	60	0·5	73·5	6
β-Methylpentenoic	αβ	60	0·33	58·3	26
	βγ	60	0·25	58·5	26

The positions of equilibrium between the pairs of acids in boiling potassium hydroxide solution * are therefore :

*cyclo*Hexane acids	12·0 ± 0·8% αβ	88 ∓ 0·8% βγ
β-Ethylpentenoic acids	5% αβ	95% βγ
β-Methylpentenoic acids	26% αβ	74% βγ

---

* The effect of alterations in the conditions on the position of equilibrium will be discussed in a future paper.

These are genuine equilibria in that they can be reached from either side and are unchanged by further action. Beesley, Ingold, and Thorpe (J., 1915, **107**, 1081), who first observed the change of *cyclo*hexylideneacetic acid into Δ^1-*cyclo*hexenylacetic acid, described it as complete and irreversible. That statement is, however, easily explained when it is remembered that the *cyclo*hexenyl acid separates from the equilibrium mixture in a solid form and, on the small scale on which those investigators worked, the 12% of αβ-acid might easily escape detection. As a result of the earlier work on the equilibration of the substituted pentenoic acids, Kon and Linstead (*loc. cit.*) stated that, whereas in the β-ethyl series the conversion of the αβ- into the βγ-form was apparently complete, in the β-methyl series the equilibrium was further on the side of the αβ-acid, although the βγ- still preponderated. The figures now obtained confirm this earlier work in all respects.

A curious feature of the present work is that equilibrium is reached in about 20 minutes in the substituted pentenoic acids, but only in an hour in the *cyclo*hexane acids. Thus the aliphatic acids appear to be the more mobile, although in the corresponding ketones the reverse is true.

The author wishes to thank Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in the progress of this research. His thanks are also due to the Government Grant Committee of the Royal Society for a grant which has largely defrayed its cost.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, November 5th*, 1926.]

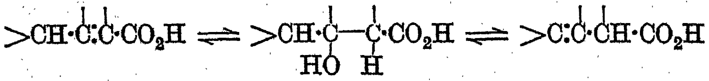
LVI.—*The Chemistry of the Three-carbon System. Part XI. The Mechanism of Isomeric Change in Unsaturated Acids.*

By REGINALD PATRICK LINSTEAD.

TAUTOMERIC compounds with retarded mobility may be regarded from the structural standpoint as insufficiently activated for complete mobility, or from the kinetic standpoint their inertia may be attributed to the infinitesimal velocities of the interconversion reactions under ordinary conditions. In such compounds, isomeric change can occur only in the presence of more or less powerful reagents, and it is this peculiarity which has led to some doubt being cast on the genuineness of the tautomerism exhibited by them. It is held that such changes can be accounted for by the addition and splitting off of the catalyst. Support is given to these views by the production, side by side with the isomeric changes, of addition compounds which could function as such intermediates. Thus Butlerov (*Annalen*, 1877, **189**, 44) and Fittig (*ibid.*, 1894, **283**, 47) have observed the addition of water during changes in unsaturated hydrocarbons and acids, and Farmer that of methyl alcohol in the dihydromuconic esters (J., 1923, **123**, 3324). The ease with which a base may function in this way is shown by the work of Ruhemann (J., 1898, **73**, 723), who observed the readiness with which these substances can be added to unsaturated systems. Only in one example has it been shown that the addition product actually formed is not that which could act as a catalyst (Ingold, Shoppee, and Thorpe, J., 1926, 1477).

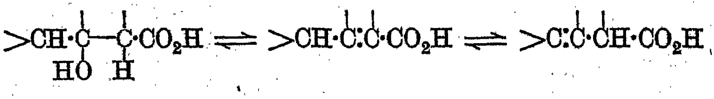
The interconversion of unsaturated acids in the presence of alkali furnishes a good example of retarded isomeric changes for the explanation of which two mechanisms can be suggested: (A) the β-hydroxy-acid functions as an intermediate product and the change proceeds by the addition and splitting off of water, or (B) tautomeric change occurs between the αβ- and the βγ-unsaturated acid, and at the same time water can be added to the αβ-acid to give the β-hydroxy-acid, the process being reversible. Fittig (*loc. cit.*), who first observed the change and the simultaneous formation of the β-hydroxy-acid, was unable to decide between these mechanisms, and with the exception of Knoevenagel's application of the Thiele hypothesis to the change (*Annalen*, 1900, **311**, 217) little further work appears to have been done either on the clearing up of this point or on the reaction as a whole.

(A)



$$>CH\cdot\overset{|}{C}:\overset{|}{C}\cdot CO_2H \rightleftharpoons >CH\cdot\underset{HO}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}\cdot CO_2H \rightleftharpoons >C:\overset{|}{C}\cdot\overset{|}{C}H\cdot CO_2H$$

(B)



$$>CH\cdot\underset{HO}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}\cdot CO_2H \rightleftharpoons >CH\cdot\overset{|}{C}:\overset{|}{C}\cdot CO_2H \rightleftharpoons >C:\overset{|}{C}\cdot\overset{|}{C}H\cdot CO_2H$$

If the tautomeric explanation (B) is correct, evidence in its favour will be forthcoming only when the additive reaction is very slow in comparison with the direct isomeric change. For example, if interconversion can be shown to occur under conditions which preclude the possibility of the presence of the β-hydroxy-acid, or the possibility of its dehydration is present, the tautomeric hypothesis will receive strong support. In some of the work of Fittig (*Annalen*, 1894, **283**, 68, 132, 297), examples of acids can be found which cast doubt on the water-addition hypothesis. Thus the pentenoic and *iso*heptenoic acids undergo interconversion under conditions in which the β-hydroxy-acid is comparatively stable, whilst in the γ-phenylbutenoic acids the conversion of the βγ- into the αβ-form stops at a definite point and further action of alkali causes an increased addition of water without affecting this equilibrium (compare Linstead and Williams, J., 1926, 2736).

The interconversion of Δ^1-*cyclo*hexenylacetic acid and *cyclo*hexylideneacetic acid now to be described is particularly suitable for investigation, as both the unsaturated acids and the corresponding β-hydroxy-acid, *cyclo*hexanolacetic acid, $C_5H_{10}{>}C(OH){\cdot}CH_2{\cdot}CO_2H$, are easily prepared and are crystalline, and the addition of water to the unsaturated system is extremely slow, the condition given above thus being satisfied.

Whilst the βγ- is the more stable form, the αβ- has considerable stability; *e.g.*, the sodium salt of the αβ-acid resists interconversion in neutral solvents even at high temperatures, and the acid itself is unaffected by sodium bicarbonate and piperidine. It is only in the presence of hot alkali hydroxides that movement of the bond can occur.

The study of the action of alkalis on the three acids is complicated by the fact that the β-hydroxy-acid readily undergoes hydrolytic fission in the presence of boiling potassium hydroxide solution with the formation of *cyclo*hexanone and potassium acetate: $C_5H_{10}{>}C(OH){\cdot}CH_2{\cdot}CO_2H \longrightarrow C_5H_{10}{>}CO + CH_3{\cdot}CO_2K$. The unsaturated acids yield these products only after more prolonged boiling with alkali, and it may therefore be supposed that addition of water to them precedes fission. The results resemble those obtained by Farrow and Kon (J., 1926, 2131) for some related unsaturated ketones.

The reactions were examined quantitatively under various conditions by the methods given on p. 369. After the requisite time of reaction, the product was divided in the usual way into a neutral fraction, containing the *cyclo*hexanone, and an acid fraction, containing any or all of the four possible acids. The acetic acid was readily separated owing to its volatility, and the *cyclo*hexanolacetic acid by its insolubility in light petroleum, in which the unsaturated acids are soluble. The unsaturated acids were estimated by the bromine addition method (preceding paper). The results are in Table I.

Some of the interconversion results obtained with the unsaturated

TABLE I.

Action of potassium hydroxide solution on cyclo*hexanolacetic acid.*

% KOH.	Time (hrs.).	Temp.	Composition of product (as % of initial material). Unchanged acid.	Unsaturated acid.*	*cyclo*-Hexanone.	Acetic acid.	% Loss.
1	48	b. p.	84·6	2·5	0	0	12·9
,,	100	,,	86·8	1·1	,,	,,	12·1
10	1	,,	92·0	4·3	,,	,,	3·7
,,	24	,,	85·2	2·7	trace	,,	12·1
60	24	20°	83·4	8·4	0	,,	8·2
,,	1	b. p.	72·1	9·0	10·1; 11·3	—	8·8
,,	1·5	,,	22·9	18·1	25·6	9·0	33·4
,,	48	,,	20·0 †		36·4	25·6	43·6

* Total figure; proportion of components not estimated.

† Not separated.

TABLE II.

Action of potassium hydroxide on unsaturated acids.

(i) On *cyclo*hexylideneacetic acid.

Expt. No.	% KOH.	Time (hrs.).	Temp.	Composition of product (% initial material). αβ-Acid.	βγ-Acid.	% Loss.
1	1	24	20°	98·8	0	1·2
2	10	24	,,	96·8	0	3·2
3	,,	1	b. p.	94·0	0	6·0
4	,,	24	,,	82·2	16·8	1·0
5	20	1	,,	94·8	2·9	2·3
6	30	1	,,	81·8	14·4	3·8
7	40	0·25	,,	93·3	6·4	0·3
8	,,	1	,,	55·3	28·5	16·2
9	,,	24	,,	12·5	83·3	4·2
10	50	0·5	,,	61·5	31·7	6·8
11	,,	1	,,	23·5	70·5	6·0
12	,,	1·55	,,	12·7	84·9	2·4
13	,,	24	,,	10·5	84·5	5·0
14	60	0·25	,,	74·5	22·7	2·8
15	,,	0·5	,,	19·9	58·1	22·0
16	,,	0·83	,,	15·7	76·7	7·6
17	,,	1	,,	12·5	83·5	4·0
18	,,	24	,,	8·0	64·4	25·2
(ii) On Δ^1-*cyclo*hexenylacetic acid.						
19	10	1	b. p.	0	94·2	5·8
20	40	1	,,	0	90·6	9·4
21	,,	24	,,	12·2	81·4	6·4
22	50	1	,,	7·8	78·2	14·2 *
23	,,	24	,,	12·4	82·6	5·0
24	60	1	,,	7·0	63·4	29·6 *
25	,,	23	,,	7·9	63·9	26·3 *

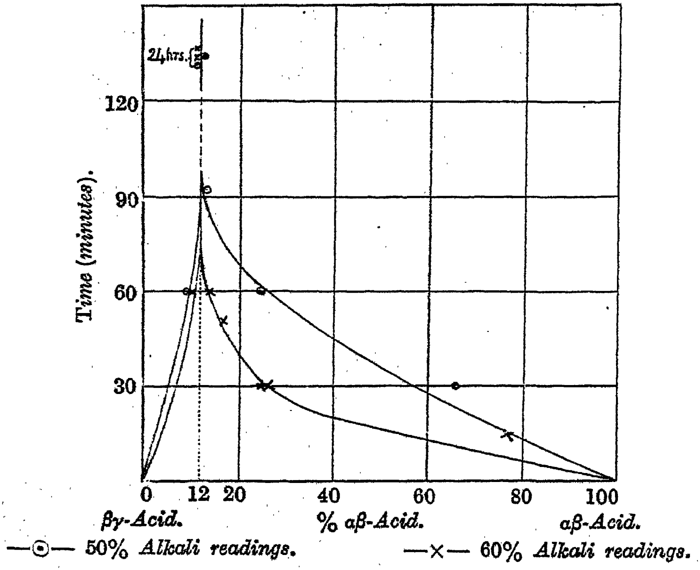
In experiment 18, the product also contained a trace of the β-hydroxy-acid, 2·6% of *cyclo*hexanone, and 1·6% of acetic acid. In experiment 25, the quantities of the same three products were a trace, 0·4%, and 2·9%, respectively. Traces of the β-hydroxy-acid were detected in experiments 22 and 24.

* Acid product distilled.

acids are given graphically in Fig. 1, where the percentage of αβ-acid in the mixture is plotted against time. The asymptotic approach to equilibrium is clearly shown.

The first point of interest that emerges from the results is the small loss which is experienced throughout, except where a large amount of fission has occurred, and in those experiments where the acid product was distilled under reduced pressure. This ensures the trustworthiness of the results as a whole. In the experiments on the unsaturated acids, no addition of water occurred, the absence of hydroxy-acid being proved in all cases by the nascent bromine method (see preceding paper). The slow rate of hydration is clearly shown by the results of some of the experiments with 60% alkali acting for 23 or 24 hours, where 36% of fission takes place from the hydroxy-acid, but only 2—3% when the unsaturated acids are used. This may possibly be due to the slowness with which the negative hydroxyl ion is added to the ion of the dissociated salt of the acid (compare Higginbotham and Lapworth, J., 1922, **121**, 49). The steric effect of the *cyclo*hexane ring also may inhibit addition. The absence of β-hydroxy-acid from the final product cannot in itself be taken as a proof that the acid does not intervene in the isomerisation, but it is clear from some of the above results that if it were formed it could not be dehydrated in quantity sufficient to account for the rapid interconversion of the unsaturated

FIG. 1.



acids. Thus the 1-hour readings with 60% alkali show that 84% of interconversion occurs under conditions in which only 9% of hydroxy-acid is dehydrated, and the 24-hour readings with 10% alkali show that 17% of interconversion occurs where the β-hydroxy-acid is almost completely unaffected.

Under ideal conditions, the interconversion reaction should be unimolecular if it is due to tautomerism and bimolecular if dependent on the addition and splitting off of water. In an infinite excess of water, however, the rate of interconversion would depend only on the concentration of the acid, whichever mechanism were true. Experimental evidence on this point, therefore, can hardly be conclusive, for a considerable excess of water was present, even in the 60% alkali experiments, where the molecular proportions of acid, potassium hydroxide, and water were 1 : 10 : 20·7.

The kinetics of unimolecular reversible reactions have been investigated by Küster (*Z. physikal. Chem.*, 1895, **18**, 171) and by Lowry (J., 1899, **75**, 224), and the equation proposed by Küster has been successfully applied to tautomeric equilibria. This connects the change in concentration of the substance, A, initially present (x) with the time (t) by the expression

$$t(k_1 + k_2) = \log_e\{\xi/(\xi - x)\} \quad . \quad . \quad . \quad . \quad (1)$$

where ξ is the value of x at equilibrium and k_1 and k_2 are the velocity coefficients of the forward and the back reaction respectively. The values of k_1 and k_2 can then be found from the equilibrium values for the concentration of A :

$$K = k_1/k_2 = \xi/(a - \xi) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a is the initial concentration of A.

The equilibrium in the pair of acids now under discussion being taken as 12% αβ-acid $\rightleftharpoons$ 88% βγ-acid (see preceding paper), the application of the Küster equation gives the results in Table III.

TABLE III.

60% Alkali (ten times the quantity required for neutralisation).

Concentrations in g./c.c. Time in minutes.

A.	t.	x.	$\xi - x$.	$k_1 + k_2$.
αβ-Acid	15	0·0865	0·2444	(0·020)
,,	30	0·2801	0·0508	0·062
,,	50	0·3121	0·0188	0·057
,,	60	0·3271	0·0038	0·075
βγ-Acid	60	0·0376	0·0075	0·068
50% Alkali (ten times the quantity required for neutralisation).				
αβ-Acid	30	0·0850	0·1351	(0·016)
,,	60	0·1875	0·0326	0·032
,,	93	0·2150	0·0051	0·040

When the severe conditions and the powerful nature of the catalyst are taken into consideration, the agreement between the figures for the constants must be regarded as good.

The individual values of k_1 and k_2 can be calculated from equation (2), the mean values for $k_1 + k_2$, 0·066 (60% alkali) and 0·036 (50% alkali), and the known value, 88 : 12, for the ratio of the quantities of the acids at equilibrium, being used. These are :

% Alkali	60%	50%
$k_1(\alpha\beta \longrightarrow \beta\gamma)$	0·058	0·032
$k_2(\beta\gamma \longrightarrow \alpha\beta)$	0·008	0·004

These figures furnish the first quantitative values for the mobility of a system of this type under specified conditions. Comparison between them and similar figures for other series would be of real significance in the study, *e.g.*, of the effect of positive groups on mobility. For such a purpose the conditions of the equilibration would have to be standardised—those used in the present work would be unsuitable because (1) the concentrations of the reagents are so high that in many series dissolution of the potassium salt would probably be incomplete, and the presence of a solid phase would affect the determinations of reaction velocity (the potassium salts of the two *cyclo*hexane acids are only just dissolved by the boiling 60% alkali solution) ; (2) the unstable acids might decompose at the high reaction temperature ; (3) the change in the *cyclo*hexane series is comparatively slow (see preceding paper). In a very mobile series the change might proceed at a rate too fast for experimental measurement, under the conditions which produce complete equilibration in some 65 minutes in the present series.

By decreasing the concentrations of the reactants and reducing the severity of the reaction, it is hoped to arrive at a standard set of conditions capable of general use.

The Effect of Conditions on Interconversion.

The experimental results show that the rate of isomeric change depends on the concentration of alkali. This may function in two ways. In the first place, increase in alkali concentration decreases the amount of water and increases the concentration of the potassium salt of the acid. Secondly, the experiments are carried out at the boiling point of the solution, and this rises with increasing concentration, the 60% solution boiling at about 145°. The experimental figures available do not at present allow of a distinction being made between the temperature and the concentration effects. The concentration of alkali does not appear to have any effect on the ultimate position of equilibrium, as there is close agreement between the results obtained with 40, 50, and 60% alkali (compare preceding paper). Johnson and Kon (J., 1926, 2748) reached the same conclusion in their investigation on the movement of the double bond in substituted cinnamic acids. From the theoretical standpoint this is unexpected, as change in temperature should displace the equilibrium in all systems except those in which the heat of reaction is zero for the tautomeric change. Küster (*loc. cit.*) showed that the position of equilibrium between the isomeric keto-pentachloro*cyclo*pentenes was considerably affected by temperature. A more accurate experimental method for the study of these and similar isomeric changes at constant temperature has now been devised and the influence of temperature on these reactions is being studied.

The Mechanism of the Reaction.

The experimental results already described provide strong support for the tautomeric nature of the reaction, but the inner mechanism of such a change is not yet clear. It can be interpreted on the lines suggested by Ingold, Shoppee, and Thorpe's application of Robinson's theory (*loc. cit.*) as an example of a highly polar catalyst facilitating the removal of the mobile hydrogen atom from the system in the form of a proton. This new hypothesis, whilst accounting for many of the experimental facts, would appear to disregard the close connexion between the enolising power of activating groups and mobility (compare Farrow and Kon, J., 1926, 2128).

EXPERIMENTAL.

Materials.—The acids used were prepared by the methods given in the preceding paper, and had the properties recorded there. *cyclo*Hexanolacetic acid was prepared by Wallach's method (*Annalen*, 1906, **347**, 329); it crystallised from hot petroleum (b. p. 60—80°) in laminæ, m. p. 64°.

Reaction with Alkali.—The acid (5 g.) was added to a hot solution of potassium hydroxide (ten times the quantity required for neutralisation) in the requisite amount of water. Except in the experiments of very short duration, a copper reaction vessel was used, fitted with a double-surface condenser and with a soda–lime tube to eliminate carbon dioxide. The time of reaction was taken from the commencement of boiling, and at its conclusion the reaction vessel was plunged into ice and the contents were extracted with ether. The *cyclo*hexanone in the dried ethereal extract was slowly freed from solvent under a long column and was weighed and identified by conversion into its semicarbazone. The alkaline liquid was acidified, cooled, and extracted with an equal volume of ether divided in several portions, the ether being subsequently removed from the dried solution through a column. If the residue contained acetic acid, this was distilled off and estimated by titration with standard alkali. The residual acid was freed from the last traces of solvent in a good vacuum. In the experiments on *cyclo*hexanol-acetic acid, the unchanged acid invariably crystallised and was freed from unsaturated acid by washing it with petroleum (b. p. 40—60°). The insoluble acid which remained melted sharply, in all cases between 56 and 64°, and was identified by mixed melting-point determinations. The soluble, unsaturated acid was freed from solvent and weighed. The amount usually obtained was insufficient for a determination of the proportion of the isomerides. When the initial material was an unsaturated acid, the acid product was tested for hydroxy-acid by the nascent bromine method and was then examined by the bromine addition method (see preceding paper). The conditions used were: concentration, 1/60 g.-mol. per litre; solvent, carbon tetrachloride; temperature, 25°. The compositions of the mixtures were found by reference to the standard curves. In some of the earlier experiments, the product was distilled under reduced pressure before examination, but this resulted in loss and served no useful purpose.

The results of these observations are in Tables I and II. The accuracy of the methods of extraction and estimation was checked by blank experiments; *e.g.*, under the conditions used, 85% of the *cyclo*hexanone was recovered and the figures given in the tables are therefore the experimental figures multiplied by a factor (1·2). Similarly, 95% of the hydroxy-acid can be isolated by the petroleum separation method mentioned above, giving a factor of 1·05, which has been used in compiling the tables. One of the analyses of the mixed unsaturated acids was kindly checked by Mr. C. J. May by Bougault's method; the results are given below.

	% βγ-Acid found.	% αβ-Acid found.	% Loss.
By bromine method	81·8	14·4	3·8
By Bougault's method	77·9	18·3	3·8

The quantitative separation of mixtures of the unsaturated acids and of several of their salts by fractional crystallisation from a variety of solvents was attempted, but no process was discovered of sufficient accuracy to check the figures obtained by the bromine method.

Sodium cyclo*hexylideneacetate* was prepared in theoretical yield by the action of "molecular" sodium on the acid in benzene solution. The gelatinous product was washed with ether and dried.

The pure salt forms fine, white needles, m. p. 276° (decomp.), from ethyl alcohol (Found: Na, 13·9. $C_8H_{11}O_2Na$ requires Na, 14·2%). It is insoluble in most organic solvents, soluble in water, and very soluble in methyl alcohol.

The pure salt was unaffected after being boiled with xylene, alcohol or water for 24 hours; pure *cyclo*hexylideneacetic acid was obtained on acidification.

The author's thanks are due to Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in the progress of this research, and to the Royal Society for a grant which has largely defrayed its cost.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, November 5th, 1926*].

LVII.—iso*Erucic Acid.*

By TAHILRAM JETHANAND MIRCHANDANI and JOHN LIONEL SIMONSEN.

*iso*ERUCIC acid was first obtained by Alexandrov and Saytzev (*J. pr. Chem.*, 1894, **49**, 58) by treating iodobehenic acid, prepared from erucic acid, with potassium hydroxide. Saytzev (*ibid.*, 1894, **50**, 65) showed that it also resulted when brassidic acid was converted into iodobehenic acid and the halogen acid treated with alkali. *iso*Erucic acid, m. p. 54—56°, was characterised by the preparation of a dibromobehenic acid, m. p. 44—46°, and by oxidation in alkaline solution with potassium permanganate to a dihydroxybehenic acid, m. p. 86—88°. At the time of these investigations, erucic acid was considered to have the constitution (I), and the above-mentioned authors regarded it as probable that *iso*erucic acid was the structural isomeride (II).

$$\text{(I.)}\ CH_3\cdot[CH_2]_{17}\cdot CH{:}CH\cdot CH_2\cdot CO_2H \quad CH_3\cdot[CH_2]_{18}\cdot CH{:}CH\cdot CO_2H\ \text{(II.)}$$

$$\text{(III.)}\ CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_{11}\cdot CO_2H$$

It was subsequently established that erucic acid and brassidic acid were the *cis*- and *trans*-modifications respectively of an acid (III), since on oxidation with ozone, followed by chromic acid, they both yielded brassylic and pelargonic acids (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1074; Jegorov, *J. pr. Chem.*, 1912, **86**, 539). The view of Alexandrov and Saytzev (*loc. cit.*) being accepted, it followed that *iso*erucic acid would in all probability have either formula (VI) or (VII), depending on whether iodobehenic acid from erucic and brassidic acids had formula (IV) or (V).

(IV.) $CH_3\cdot[CH_2]_6\cdot CH_2\cdot CHI\cdot[CH_2]_{12}\cdot CO_2H$

(V.) $CH_3\cdot[CH_2]_8\cdot CHI\cdot CH_2\cdot[CH_2]_{10}\cdot CO_2H$

(VI.) $CH_3\cdot[CH_2]_6\cdot CH\colon CH\cdot[CH_2]_{12}\cdot CO_2H$

(VII.) $CH_3\cdot[CH_2]_8\cdot CH\colon CH\cdot[CH_2]_{10}\cdot CO_2H$

It was shown, however, by Ponzio (*Gazzetta*, 1904, **34**, ii, 50) that when *iso*erucic acid was oxidised by concentrated nitric acid, in a manner similar to that used in the oxidation of erucic acid (*J. pr. Chem.*, 1893, **48**, 323), it gave a mixture of acids from which brassylic and pelargonic acids were isolated and he showed further that the dibromo-acid (m. p. 44—46°), on treatment with alkali, yielded a behenolic acid identical with that obtained under the same conditions from the dibromo-acids derived from erucic and brassidic acids. As a result of these experiments he very legitimately concluded that *iso*erucic acid was not a structural isomeride of erucic and brassidic acids. In subsequent years, a number of investigations were carried out with the object of determining by physico-chemical methods the relationship of these three acids (Mascarelli and Toschi, *Gazzetta*, 1915, **45**, i, 314; Mascarelli and Sanna, *ibid.*, 1915, **45**, ii, 208, 315; Mascarelli, *ibid.*, 1917, **47**, i, 160). The conclusion was reached that in all probability brassidic and *iso*erucic acids were dimorphic forms of the *trans*-acid (III), but all attempts to convert one acid into the other failed.

Notwithstanding Ponzio's experiments, it appeared to us possible that the original view of Alexandrov and Saytzev might be correct, since the oxidation of an unsaturated fatty acid with concentrated nitric acid, owing to the extreme violence with which it proceeds, cannot be regarded as an entirely satisfactory method of orienting a double linking, whilst the conversion of the dibromobehenic acid into the acetylenic acid is carried out under conditions which are recognised as favourable to isomeric change.

Repetition of the oxidation of *iso*erucic acid with nitric acid has confirmed the formation of brassylic acid as one of the products of the reaction, but the yield of this dibasic acid is extremely small, the main substances formed being acids of lower molecular weight. We decided, therefore, to oxidise *iso*erucic acid, in the form of its ester, with ozone and also with potassium permanganate under the standard conditions used by Armstrong and Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 43 T) for the oxidation of methyl oleate.

The *iso*erucic acid used in these experiments was prepared by the method of Alexandrov and Saytzev (*loc. cit.*) and purified by repeated crystallisation from alcohol (95%). It melted sharply at 55—57° and appeared to be homogeneous. Treatment of the *ethyl* ester with ozone gave, in addition to the main oxidation products, which will be discussed later, a not inconsiderable quantity of ethyl arachidate. There is no doubt that the *iso*erucic acid used in the earlier experiments was contaminated with arachidic acid, although the acid had the correct m. p. and crystallised extremely well. In our later experiments, the *iso*erucic acid, after crystallisation from alcohol to constant melting point, was further purified by fractional precipitation of the zinc salt, and any arachidic acid was thus removed in the least soluble fractions.

When ethyl *iso*erucate was oxidised with ozone, under conditions which, with erucic acid, were found to yield a readily separable mixture of brassylic and pelargonic acids (see p. 376), the oxidation product was a mixture which was somewhat difficult to resolve. As the quantity of this material was limited, we examined only the mixture of dibasic acids formed. We were able to isolate (*a*) decane-$\alpha\kappa$-dicarboxylic acid, $HO_2C\cdot[CH_2]_{10}\cdot CO_2H$, m. p. 126—127°, identified by comparison with a synthetic specimen of the acid (Walker and Lumsden, J., 1901, 79, 1201), and (*b*) dodecane-$\alpha\mu$-dicarboxylic acid, $HO_2C\cdot[CH_2]_{12}\cdot CO_2H$, m. p. 121—122°, identified by analysis and by preparation of the methyl ester, m. p. 41°.

This result of the oxidation of ethyl *iso*erucate with ozone was surprising, and appeared to show that *iso*erucic acid, in spite of its sharp m. p. and well-defined crystalline form, was not homogeneous but was a mixture of the two unsaturated acids (VI) and (VII).

To confirm this conclusion, a quantity of very carefully purified methyl *iso*erucate was oxidised in acetone solution with potassium permanganate. From the oxidation products we were able to separate the two dibasic acids mentioned above and also *n*-octoic acid. Unfortunately, *n*-decoic acid, which must also have been formed, could not be obtained in a pure state.

This experiment confirmed in all respects the results obtained by oxidation with ozone and seems to leave no doubt that *iso*erucic acid is not a homogeneous substance, but is a mixture of Δ^{11}-*docosene*-1-*carboxylic acid* and Δ^{13}-*docosene*-1-*carboxylic acid*. From the yields of the oxidation acids the two acids would appear to be present in approximately equal amounts.

Since *iso*erucic acid itself was an inseparable mixture, we examined a number of derivatives to see whether any of them showed signs of heterogeneity. The *methyl* ester is crystalline, m. p. 24—26°, resolidifying at 22°; the *anilide* and p-*toluidide* both crystallise extremely well and both before and after crystallisation have the same m. p.; the *zinc* salt appears to be homogeneous.

As has already been mentioned, *iso*erucic acid is stated to yield a dibromo-derivative, m. p. 42—44°, or 46—46·6° according to Macbeth and Stewart (P., 1912, **28**, 68). We have repeated the preparation of this substance several times, but in every case the bromination product had the appearance of a mixture and the m. p. was not sharp. We have not tried the oxidation of *iso*erucic acid to dihydroxybehenic acid, but it is probable that this is a mixture of two dihydroxy-acids.

The fact that *iso*erucic acid is an inseparable mixture of two acids yielding apparently homogeneous derivatives is somewhat unusual, but is not unique. Attention may be directed to the following somewhat similar cases: mononitro-*o*-veratraldehyde, m. p. 88° (Perkin, Roberts, and Robinson, J., 1914, **105**, 2389), has been shown to be a mixture of two isomeric nitroveratraldehydes of m. p. 110° and 113° respectively (Perkin, Robinson, and Stoyle, J., 1924, **125**, 2355); anisic and veratric acids form a mixture, m. p. 145°, inseparable by crystallisation (Cain and Simonsen, J., 1912, **101**, 1061); the geometrical isomerides of camphorquinone-oxime (*iso*nitrosocamphor) are inseparable by solvents and produce a mixture melting higher than the more fusible modification (Forster, J., 1903, **83**, 535); benzoic and *p*-nitrobenzoic acids in the proportion 2 : 1 form a mixture indivisible by solvents and melting at 182—198° (Forster and Saville, J., 1922, **121**, 823).

During our preliminary experiments we investigated the oxidation of erucic and brassidic acids under various conditions and found the nature of the dihydroxy-acid formed to be dependent on the conditions used. In view of the recent publication of Hilditch (J., 1926, 1828) we do not intend to continue this side of the investigation. Experiments on the synthesis of the two unsaturated acids (VI and VII) are in progress and will, it is hoped, form the subject of a future communication.

EXPERIMENTAL.

*iso*Erucic acid prepared by Alexandrov and Saytzev's method (*loc. cit.*), after four crystallisations from alcohol, melted at 54—56°, but, as has already been mentioned, it was found as the result of oxidation experiments to contain a small percentage of arachidic acid. The acid was purified by fractional precipitation of the zinc salt; eight fractions were obtained, of which the first two were rejected, since they contained arachidic acid. After this purification, the acid had m. p. 55—57° and $n_D^{64^\circ}$ 1·4469.*

*iso*Erucic acid is not affected by treatment with nitrous acid under conditions which convert erucic acid into brassidic acid, nor does it

* The refractive indices of erucic and brassidic acids at the same temperature were 1·4480 and 1·4472, respectively.

undergo any change when an alcoholic solution containing a trace of iodine is exposed to bright sunlight for some days.

The *zinc* salt crystallised from benzene in thin leaflets, m. p. 109°. No depression of the m. p. occurs on admixture with an equal amount of the zinc salt of brassidic acid (m. p. 112—113°), but the crystalline forms of the two salts are different, the latter salt crystallising in needles.

The *anilide* separated from alcohol in fine needles, m. p. 77—78·5° (Found : N, 3·6. $C_{28}H_{47}ON$ requires N, 3·4%), and the p-*toluidide* in needles, m. p. 85—86° (Found : N, 3·5. $C_{29}H_{49}ON$ requires N, 3·3%).

The *methyl* ester, prepared by treating the acid with methyl alcohol and sulphuric acid, crystallised in needles, b. p. 240°/14 mm., m. p. about 24—26°, resolidifying at 22° (thermometer in liquid). It is somewhat sparingly soluble in methyl alcohol (Found : *M*, 351·1; iod. val., 71·9. $C_{23}H_{44}O_2$ requires *M*, 352; iod. val., 72). The *ethyl* ester is a viscid oil, b. p. 243°/8 mm.

Oxidation of Methyl iso*Erucate with Potassium Permanganate.*— Methyl *iso*erucate (50 g.) was dissolved in acetone (500 c.c.), and potassium permanganate (168 g.) gradually added. The oxidation proceeded vigorously and sufficient heat was generated to keep the acetone boiling. The reaction mixture was heated on the water-bath for 15 hours, the acetone distilled off, and the manganese dioxide sludge dissolved by the addition of dilute sulphuric acid and sodium bisulphite. The oil which had separated was dissolved in ether, and the ethereal extract was washed with sodium carbonate solution until no further acid was removed, dried, and evaporated (A). The sodium carbonate extract was mixed with an excess of sodium hydroxide solution, boiled for one hour, and acidified. The liberated organic acids were dissolved in ether; on removal of the solvent a semi-solid, crystalline mass remained (47 g.). The mixture of acids was digested with light petroleum (b. p. 40—60°), and the boiling solution filtered (residue B), a small quantity of solid which separated on cooling being added to B. The light-petroleum extract was evaporated and the liquid acids (20 g.) were distilled; a large fraction was then obtained, b. p. 230—270°/ 685 mm. The residue in the distilling flask (4 g.) crystallised and was added to B. On refractionation, a fraction was obtained, b. p. 232—235°/685 mm., which was identified as *n*-octoic acid by titration (Found : *M*, 146. Calc. : *M*, 144) and by preparation of the *p*-toluidide, m. p. 67—69°. This m. p. was not depressed on admixture with an authentic specimen (Found : N, 6·1. Calc. : N, 6·0%). It was not found possible to separate a constant-boiling fraction from the residue.

The solid acid (B), m. p. 80—100°, was a mixture which could not be resolved by fractional crystallisation. Preliminary experiments having shown that one of the acids yielded a magnesium salt which was readily soluble in water, the mixture of acids was dissolved in dilute sodium hydroxide solution (phenolphthalein), and the boiling solution treated with an excess of magnesium sulphate. The sparingly soluble magnesium salt, B_1, was collected after 12 hours, and the filtrate acidified; a voluminous, white precipitate then separated. This was taken up with ether (yield, 9 g.) and recrystallised from hot water and finally from ethyl acetate, flat needles being obtained (Found: C, 63·0; H, 9·6; *M*, 230·6. Calc.: C, 62·6; H, 9·5%; *M*, 230). It melted at 126—127°, alone or mixed with decane-$\alpha\kappa$-dicarboxylic acid, prepared by Walker and Lumsden's method (*loc. cit.*).

The sparingly soluble magnesium salt B_1 was decomposed with dilute sulphuric acid. The acid thus obtained (16 g.), m. p. 90—95°, softening at 80° (*M*, 255·6), was fractionally converted into the magnesium salt, four fractions being obtained. Titration showed that the last fraction, which was soluble in water, was mainly decane-$\alpha\kappa$-dicarboxylic acid (*M*, 235); this was also present in not inappreciable amount in fraction 3 (*M*, 247·4). The first two fractions (*M*, 259; 256), which were evidently identical, were combined and recrystallised from ethyl acetate; an acid then separated in leaflets, m. p. 121—122° (Found: C, 65·1; H, 10·3; *M*, 258·9. Calc.: C, 65·1; H, 10·1%; *M*, 258). The barium salt also was analysed (Found: Ba, 34·8. Calc.: Ba, 34·9%). This acid has the properties of dodecane-$\alpha\mu$-dicarboxylic acid (Brown and Walker, *Annalen*, 1891, **261**, 123); direct comparison was not possible, but the methyl ester prepared from the silver salt separated in needles, m. p. 41°, which is stated to be the m. p. of methyl dodecane-$\alpha\mu$-dicarboxylate.

The neutral oil A (see above; 9 g.) consisted of unchanged methyl *iso*erucate.

The actual yields of the oxidation acids obtained and those calculated on the assumption that *iso*erucic acid is an equimolecular mixture of the two unsaturated acids, allowance being made for the weight of methyl *iso*erucate recovered, are: monobasic acids obtained, 16 g.; calc., 17·8 g.; dibasic acids obtained, 26 g.; calc., 28·2 g.

Oxidation of Ethyl iso*Erucate with Ozone.*—In a preliminary experiment made with the object of determining the most suitable conditions for the oxidation of ethyl *iso*erucate, erucic acid (10 g.) was oxidised with ozone, followed by chromic acid, under the conditions described below. The mixture of acids was taken up with ether and on removal of the solvent an oil was obtained which partly crystallised. The solid, which melted at 109° after being washed with light petroleum and at 112—113° after crystallisation from benzene, was identified as brassylic acid by the method of mixed m. p. and by titration (Found: *M*, 243. Calc.: *M*, 244). The original filtrate, on dilution with light petroleum, deposited a further quantity of brassylic acid (m. p. 110°), and after the removal of this it was fractionated, b. p. 249—252°/685 mm., leaving a small residue which crystallised and probably consisted of brassylic acid, but was not further examined. The distillate was identified as pelargonic acid by titration (Found: *M*, 159·5. Calc.: *M*, 158).

Ozone was passed through a well-cooled solution of ethyl *iso*erucate (10 g.) in acetic acid (70 c.c.) until a test portion no longer decolorised bromine. After the addition of formic acid (10 c.c.), the solution was heated on the water-bath for 2 hours, cooled, and treated with an aqueous solution of chromic acid sufficient in quantity to convert the aldehydes present into the corresponding carboxylic acids. The mixture of acids (from 30 g. of ethyl *iso*erucate) was dissolved in ether and, after removal of the solvent, converted into the ethyl esters. On distillation under diminished pressure (8 mm.), the following fractions were obtained: (i) up to 150° (14 g.), (ii) 150—180° (5 g.), (iii) 180—190° (8 g.), (iv) 190—210° (6 g.), (v) above 210° (3 g.). Fraction (i) consisted of the esters of the monobasic acids and was not further examined; fraction (v) crystallised on keeping and was identified as ethyl arachidate, m. p. 50° (m. p. of acid, 77°) (Found: *M*, 311. Calc.: *M*, 312).

Since on redistillation the intermediate fractions could not be obtained pure, they were combined and after hydrolysis the acids were separated by the magnesium salt method described above. The fractions of the soluble and the insoluble magnesium salts were converted into the methyl esters through the silver salts; the soluble magnesium salt then yielded a methyl ester, b. p. 175—177°/10 mm. This was *methyl decane-$\alpha\kappa$-dicarboxylate*, since on hydrolysis it gave decane-$\alpha\kappa$-dicarboxylic acid, m. p. 126—127° (Found: *M*, 230·6. Calc.: *M*, 230).

The methyl ester from the acid yielding the sparingly soluble magnesium salt distilled at 191—192°/10 mm. and solidified on keeping; it melted at 41° after crystallisation from methyl alcohol. The acid obtained on hydrolysis had m. p. 121° (Found: *M*, 257·6. Calc.: *M*, 258).

Oxidation of Erucic and Brassidic Acids.—Erucic acid, on oxidation in alkaline solution under the conditions used by Lapworth and Mottram (J., 1925, **127**, 1629) for oleic acid, gave the high-melting dihydroxybehenic acid (m. p. 127—128°; yield 36%). In cold acetone solution, it gave the low-melting isomeride, m. p. 99—100°. Under similar conditions, brassidic acid yielded only the low-melting dihydroxy-acid.

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BANGALORE. [*Received, October 18th, 1926.*]

LVIII.—*Overpotential at Antimony Cathodes and Electrolytic Stibine Formation.*

By HENRY J. S. SAND, JULIUS GRANT, and WILLIAM VERNON LLOYD.

As is well known, two methods yielding different results are in common use for the measurement of electrolytic polarisation, *viz.*, the " direct " and the " commutator " method. In the former, the *P.D.* between the working electrode and the liquid in immediate contact with it is measured *during* the passage of the current and compared with that found in the absence of current; in the latter, the same *P.D.* is measured as soon as possible *after* interrupting the current. The attitude taken up by one of us (H. J. S. S.) to results obtained by the former method has been that only that portion of the measured *P.D.* should be considered to be a polarisation which is definitely proved to be so by the latter method. To indicate this attitude, the term *transfer-resistance* introduced by Gore (*Proc. Roy. Soc.*, 1885, **38**, 209; also numerous papers in *Phil. Mag.*) was revived in 1909 by Sand and Black (*Z. physikal. Chem.*, 1910, **70**, 496). This term has since been extensively used by Newbery (*Trans. Faraday Soc.*, 1919, **15**, 126) and others. The term may appear to imply definitely the irreversible character of the phenomenon measured, and, in so far as its unknown character was primarily to be indicated, it is now recognised that the term *transfer-impedance* would better comprise both reversible and irreversible effects. Both the direct and the commutator method have been extensively criticised without finality having been reached; but it is remarkable that very little attention has been hitherto directed to the entirely different character of the results obtained by the two methods. Whilst the direct method appears to lead to the conclusion that polarisation increases indefinitely with *C.D.*, the commutator method always yields results which point definitely to the existence of a maximum of polarisation. Experiments are now recorded which were carried out to determine whether there is any indication in the current density–polarisation (overvoltage) curves, determined by the direct method, of the polarisation-maxima shown by the commutator method.

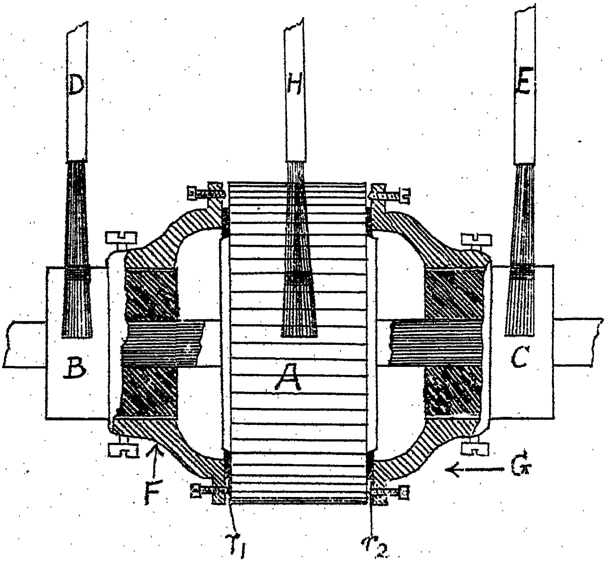
EXPERIMENTAL.

An antimony electrode was used as in previous work (Sand, Weeks, and Worrell, J., 1923, **123**, 456; Sand and Weeks, J., 1924, **125**, 160). An advantage of this metal is that it allows the phenomenon of polarisation to be studied in conjunction with that of hydride formation. The experiments reported by Sand, Weeks, and Worrell (*loc. cit.*) were repeated. We very much regret that we have been unable to confirm the numerous and detailed reports of his experiments supplied by Mr. Worrell, even when working with the same materials and apparatus. We are unable to account for these reports and wish to sever all association with them. The reports furnished by Mr. Weeks we have confirmed in general outline, but not in detail. The experimental arrangements used have been in part further developed for the purposes of the present investigation. The electrolytes employed were: (1) Solutions of various acids in varying concentrations; (2) solutions of acids containing salts; and (3) solutions of alkaline substances.

The main points studied have been (1) the dependence of polarisation on the time which has elapsed since the breaking of the current; (2) the relation between the overvoltage–current density curves for a given solution and electrode, determined on the one hand by the direct and on the other by the commutator method; (3) the relation between the values obtained and the composition of the solution, including hydrogen-ion concentration; and (4) the dependence of hydride formation on the conditions of the experiment. The first point has been studied for other electrodes by a number of workers (Glasstone, J., 1923, **123**, 2926; 1924, **125**, 250, 2646; 1925, **127**, 1824; *Trans. Faraday Soc.*, 1924, **19**, 808; Knobel, *J. Amer. Chem. Soc.*, 1924, **46**, 2613; Newbery, J., 1924, **125**, 511; *Proc. Roy. Soc.*, 1925, *A*, **107**, 486; 1926, *A*, **111**, 182). Whereas Glasstone and Knobel employed mechanical commutators, Newbery used the cathode-ray oscillograph. The method employed in the present investigation belongs to the class employed by the first-named authors, but the apparatus allows readings to be made after very much shorter time-intervals than have been hitherto attempted.

Figs. 1*a* and 1*b* illustrate the principle of the commutator employed. In the design and construction of this instrument we have had the assistance of Messrs. F. S. M. and J. F. Wright, of Messrs. F. Cox, Ltd., which we gratefully acknowledge. The apparatus consists essentially of a 64-segment dynamo commutator of commercial construction, A, which was mounted on the same spindle with two insulated slip-rings, B and C, the latter being in communication through the wire brushes, D and E, with the source of current and the potentiometer, respectively. To each slip-ring was screwed a cup-shaped casting, F and G, each of which was supplied with 64 screw-holes and screws that were placed opposite the 64 segments of the commutator. It was thus possible to bring any one segment into electrical communication with either or both of the slip-rings. These castings were spaced relatively to the central commutator by means of the rubber rings, r_1 and r_2. The commutator brush, H, was connected to the working electrode, and it was thus possible to connect the latter during time-intervals equal to that of 1/64 of a revolution to either the source of current or the potentiometer. Thus, if 32 successive segments were connected to the current slip-ring B, 32 being left unconnected to B; if, further, these latter were connected individually in successive experiments to the potentiometer slip-ring C; and if the number of revolutions of the commutator was r per min., the current would pass through the cathode during $32/64r$ min. and would be off for an equal time, during which the average cathode potential could be measured in intervals of $1/64r$ min. An ordinary bearing was at first employed but, later, ball-bearings were fitted. The spindle of the commutator was driven by means of a pulley and belt from an electric motor, and the drive was sufficiently powerful to allow a speed counter to be pushed against the spindle without slowing it

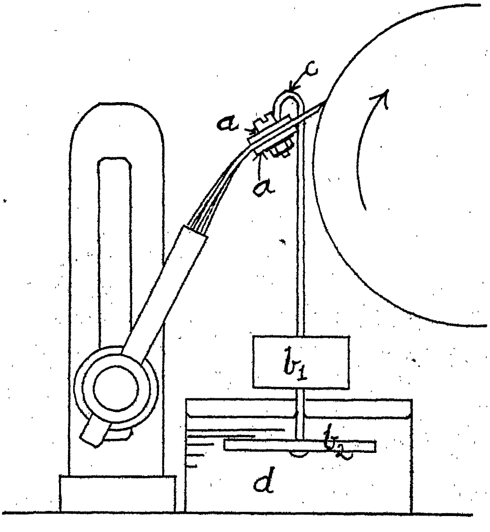
Fig. 1a.



down appreciably. The speed at which the instrument was run in many of the experiments recorded was 4200 revs. per min.

The main difficulty encountered was due to electrical leakage. General electric leakage from outside was obviated by placing the apparatus on insulating material which lay on earthed metal plates. To prevent leakage across the segments, which was apt to occur owing to metal or other dust, it was necessary to brush out the apparatus. For this purpose, all parts of the commutator were accessible after the screws locking the castings F and G had been loosened and the latter had been pushed back. An ordinary brass wire brush, as indicated in Fig. 1*a*, was at first employed; later, however, it was replaced by a copper brush the construction of which is explained in Fig. 1*b*. This consisted of 13 copper wires, of about 16 wire-gauge, which were soldered into a brass holder and spread out into a flat band by clamping them between the two plates *a*, *a*. The wires were cut off obliquely in the manner shown, so as to form a contact along a straight line on the commutator surface. In order to prevent the brush from vibrating unduly, it was weighted by means of the weights b_1, b_2 amounting altogether to about 150 g. These were hung from *a*, *a* by means of the hook *c*, and their motion was damped by placing b_2 in oil contained in the dash pot *d*. The mica insulation between successive segments of the commutator was cut away at the top for a distance of about 1 mm. in order to obtain a sharper break. A difficulty met with when a large number of successive segments was connected simultaneously to the same slip-ring was due to the fact that tightening up one screw tended to loosen its neighbours. To obviate this, only one or two screws were employed to make the connexion to the slip-ring, and the successive segments were put into communication with each other by means of pieces of tin foil that were held down by a rubber band slipped over the commutator.

FIG. 1*b*.



The efficiency of the instrument is of the same order as that of the cathode-ray oscillograph. Thus, large numbers of experiments were carried out in which the average potential was measured during $2\cdot2 \times 10^{-4}$ sec. after the breaking of the current, which is approximately the instantaneous potential after $1\cdot1 \times 10^{-4}$ sec. The smallest times after the breaking of the current recorded by Glasstone are 20×10^{-4} sec., and the corresponding shortest time shown by Knobel in his curves is 5×10^{-4} sec.

Currents were measured in all experiments by moving-coil ammeters suitably shunted. Where intermittent current is employed, such instruments do not register the instantaneous value of the current, but act with sufficient accuracy as coulombmeters (J., 1923, **123**, 2896). It must therefore be understood that all current densities are stated in millicoulombs/sec./sq. cm., even where for brevity the term "milliamperes" is employed. Where measurements by the direct method were made in alternation with those by the commutator method, the former were carried out by introducing a short-circuit between the current slip-ring brush and the commutator brush without altering any other connexion.

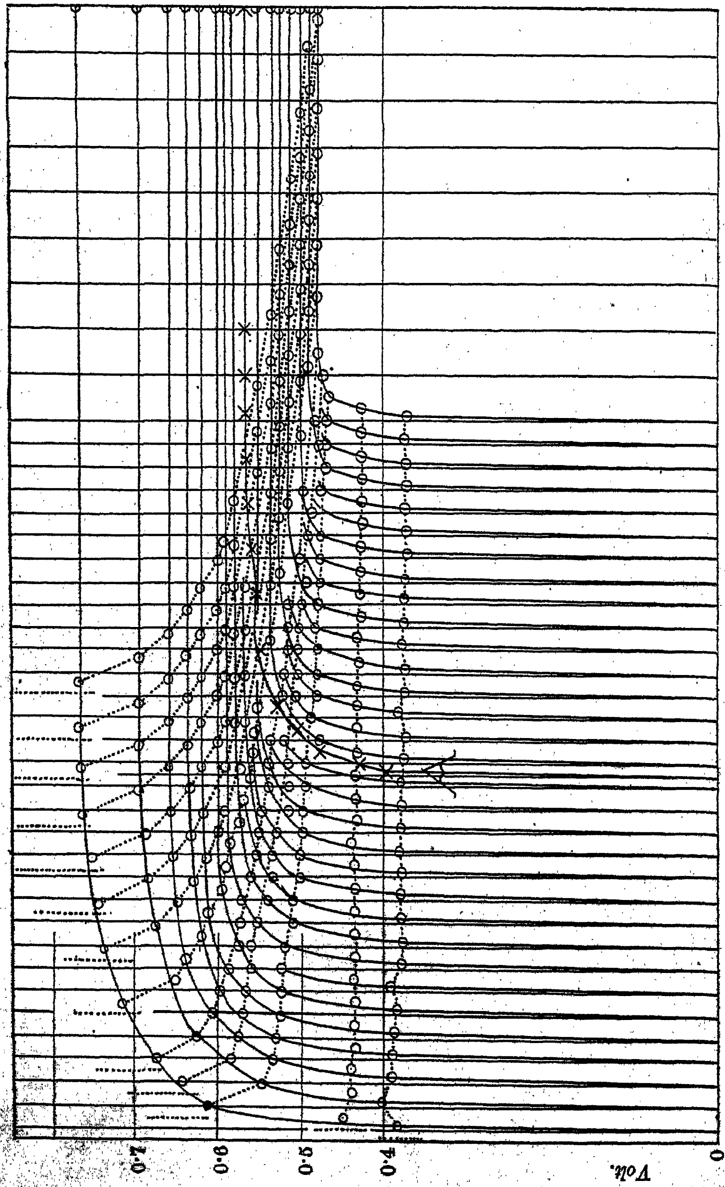
The electrolytic apparatus was approximately the same as that hitherto used, but was adapted to the measurement of the cathode potential by the direct method. As in previous work, the electrolyte in the hydrogen-electrode chamber was the same as that around the cathode. Hydrogen was kept bubbling continuously through it, and, except in some of the experiments on yields of stibine, was afterwards led past the exposed surface of the cathode. The method of measuring the yield of stibine was generally the same as that previously employed, *i.e.*, the hydrogen issuing from the cathode chamber was passed through a solution of silver nitrate and the increase of weight determined. The method might perhaps be criticised on the ground that hydrogen, even when purified carefully, is found always to precipitate small amounts of silver from silver nitrate solutions, the increase of weight thus produced being equal to that of the hydrogen absorbed. This increase was, however, negligible in all cases. Thus, in an experiment in which 1000 c.c. of dried hydrogen were bubbled slowly through the silver nitrate absorption bulbs, the total increase in these *plus* the calcium chloride tubes was found to be less than 2 mg., corresponding to a calculated volume error in the ratio of stibine to hydrogen of only about 3 parts in 10,000 parts. In many of the experiments, yields of stibine were determined by passing the issuing gas through a heated quartz tube of about 3 mm. bore and estimating the increase of weight. In no case was a perceptible difference obtained between such experiments and those in which silver nitrate solution was employed.

Results in Acid Solution. (*Experiments by* W. V. LLOYD.)

Solutions of Acids in the Absence of Salts.—Experiments were first carried out on the reproducibility of results. Most of these were performed with one of the commutators used in former work. Hydrogen was bubbled past the electrode, as previously explained. With a definite commutator speed at a given temperature, closely reproducible results were obtained. In a series of experiments it requires about 10 minutes to polarise the antimony cathode to its maximum, a *C.D.* slightly over the critical value being used. After this, results are reproducible, under carefully controlled conditions, to within a few millivolts. The material of the electrodes was purchased at various times and was the purest obtainable. Some of the antimony bars were obtained as such; others were cast from powder. A series of experiments showed that, when the antimony was suspended from platinum wires, or when platinum was wound round it, the same values of overvoltage were ultimately obtained, but these took longer to establish themselves. The antimony appeared to be very little attacked in these experiments and the surface was only very slightly dulled. The electrodes were polished by means of fine emery paper before the experiments.

A large number of readings were taken with the commutator shown in Fig. 1*a*, to determine the relation between polarisation and time for various intervals after interrupting the current, and with various *C.D.*'s. A complete study of polarisation was made in the case of *N*-, 4*N*-, and 16*N*-sulphuric acid. Thirty-two segments of the commutator were connected to the current slip-ring, and the potentiometer slip-ring was successively connected to each of the other thirty-two. The speed of the commutator was 4200 revs. per min.; the readings on the potentiometer thus represent average polarisations during $2{\cdot}2 \times 10^{-4}$ sec. and the current was alternately on and off during 1/140 sec. The results of the study of *N*-sulphuric acid have been graphically represented in Fig. 2 in such a manner as to give (1) for each segment a curve representing the relation between overvoltage and *C.D.*, and (2) for each *C.D.* a curve indicating the relation between overvoltage and time since the breaking of the current. To make this possible, all voltages are plotted as ordinates on the same scale and have the same zero. Current densities are plotted as abscissæ, likewise all on the same scale, but they start from different zeros for each segment. These zeros have been made recognisable for each current density–overvoltage curve by arbitrarily extrapolating it

FIG. 2.



Interval commutator curves: ⊖-⊖-⊖-⊖ } ←→ = 1 $\frac{\text{milliamp.}}{\text{sq. cm.}}$ *Decay curve*: ··⊙··⊙··⊙··⊙·· ←→ = 0·00044 *sec*
Average commutator curve A: ✕-✕-✕-✕ }

backwards to zero overvoltage for zero *C.D.* The current density zeros for successive segments have been placed at an equal distance from each other, and since the time interval between the polarisations on such segments was 2·2 × 10^{-4} sec., this time interval is also represented by the distance chosen. Points corresponding to overvoltages measured on successive segments for the same *C.D.*'s have therefore been connected by dotted curves which may be termed decay curves, and represent the rate of decay of overvoltage with time. The zero line of the abscissæ of each dotted curve has also been dotted in as a vertical line. The current density–overvoltage curve, corresponding to the combined effect of 30 segments simultaneously connected to the potentiometer, has been drawn for purposes of comparison half-way between the curves belonging to the two middle segments and is indicated by A. The following new facts emerge. (1) For each individual segment the polarisation rises to a maximum which it maintains constant in every case for *C.D.*'s between about 8 and 100 milliamps./sq. cm. In the case of the segments furthest removed from the break of the current, the maximum is attained at a *C.D.* below 2 milliamps./sq. cm. At *C.D.*'s above 100 milliamps./sq. cm. there is a slight decrease in polarisation, which may probably be explained by local heating. (2) The sharpest drop in polarisation occurs between the first and second segments. It is therefore unsatisfactory to extrapolate to zero time from values obtained on later segments, as advocated by Glasstone (*loc. cit.*). The first reading employed by this investigator in his studies of overvoltage of other metals corresponds approximately to the fourth point of the dotted decay curves shown in our diagram. It will be apparent from the first three additional points given here, that in the absence of an agreed equation, extrapolation leads to quite uncertain results. We therefore suggest that polarisation is best expressed by stating not only its value but also the time-interval during which it is measured. In many cases it might be sufficient to state the mean time between the beginning and end of the measurement. (3) The curves show that, when overvoltage on antimony electrodes in *N*/1-sulphuric acid does not exceed about 0·45 volt, it maintains itself sensibly constant over the whole range examined of 1/140 sec.

For the further study of polarisation, overvoltages obtained by the direct and by the commutator methods in the same solutions were compared. A thorough study was made of solutions of sulphuric acid in strengths varying from 16*N* to *N*/160; of hydrochloric acid (4*N* to *N*/16); of phosphoric acid (8*N* to *N*/16); and of *N*/1-oxalic acid. Some of the numbers obtained for *N*/1-sulphuric acid are recorded in Table I, those for the other electrolytes being similar in general character. The commutator overvoltages were obtained by means of the Whetham commutator employed in previous investigations and are average polarisations during the first 0·0059 sec. after breaking the current. Measurements by the

TABLE I.

(N-H_2SO_4.)

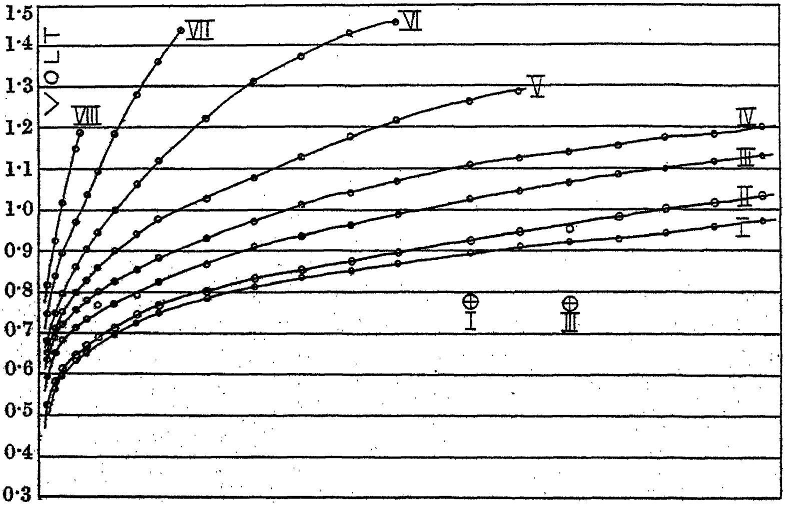
Milliamps./cm.²	0·06	0·18	0·31	0·50	0·63
Millivolts (Comm.).	322	383	415	447	467
,, (Dir.)	331	398	428	459	477
Milliamps./cm.²	0·75	0·87	0·98	3·0	4·9
Millivolts (Comm.).	483	496	509	557	559
,, (Dir.)	492	507	520	618	658
Milliamps./cm.²	6·9	8·8	11·7	17·7	21·6
Millivolts (Comm.).	559	559	559	559	559
,, (Dir.)	685	704	725	755	770
Milliamps./cm.²	25·5	29·5	43·7	70·0	87·5
Millivolts (Comm.).	558	558	556	554	554
,, (Dir.)	784	796	840	903	935
Milliamps./cm.²	105	122	140	166	184
Millivolts (Comm.).	552	552	552	550	548
,, (Dir.)	964	988	1014	1049	1075
Milliamps./cm.²	201	219	236	262	
Millivolts (Comm.).	548	546	546	546	
,, (Dir.)	1092	1106	1119	1138	

direct method were made alternately with those by the commutator method for each *C.D.* It will be seen that for low polarisations up to and slightly beyond 0·45 volt, the value previously mentioned, overvoltages measured by the direct and by the commutator method are sensibly identical, when expressed in coulombs/sec./sq. cm.

The further study of the results is best made in conjunction with Fig. 3 in which current density–overvoltage curves, obtained by the direct method, are plotted for solutions of sulphuric acid of various strengths. It will be seen that at high *C.D.*'s increases in direct overvoltages become nearly proportional to increases in *C.D.* For very high *C.D.*'s, however, such as those for which the commutator overvoltages begin to show a decrease, there is a falling off from the linear relation. The simplest way to explain this phenomenon is to assume that at high *C.D.*'s an almost constant transfer- (or surface) resistance establishes itself, which, however, shows a tendency to decrease with increase of the *C.D.* to extremely high values. The overvoltage measured should then be equal to the sum of a true polarisation ω, plus a term $i\kappa$, where ω is a value approaching the commutator overvoltage extrapolated to zero time-interval, i is the current density, and κ is the transfer-resistance per unit surface. Commutator overvoltages, determined by measurement on the first segment of the interval commutator, are shown separately on the diagram for 16N- and N-acid. It can be seen that in the case of the strong solutions of sulphuric acid the commutator overvoltage thus determined is almost identical with the voltage indicated by the ordinate corresponding to zero current density on the asymptote found by the direct method. In the case of the other solutions shown, there is an approximation to a like result. Phosphoric acid solutions gave results similar to those found with sulphuric acid. In hydrochloric and oxalic acid solutions, the differences between the commutator- and the extrapolated direct-method overvoltages were considerably greater than with sulphuric and phosphoric acids.

Relation between Overvoltages and the Composition of the Solution.—To investigate this, overvoltages were determined for a large number of electrolytes by means of the Whetham commutator giving average polarisations corresponding to an interval of 0·0059 sec. after breaking the current. The maximum values (critical overvoltages) for some of the sulphuric acid solutions examined are assembled in Table II.

Fig. 3.



⟷ = 20 *milliamps./sq. cm.* ⊕ = *First segment of commutator.*

I, $16N\text{-}H_2SO_4$. II, $8N\text{-}H_2SO_4$. III, $N\text{-}H_2SO_4$. IV, $N/4\text{-}H_2SO_4$. V, $N/16\text{-}H_2SO_4$. VI, $N/32\text{-}H_2SO_4$. VII, $N/64\text{-}H_2SO_4$. VIII, $N/160\text{-}H_2SO_4$.

TABLE II.

(Sulphuric acid solutions.)

Conc.	16*N*.	8*N*.	4*N*.	2*N*.	*N*.	*N*/4.	*N*/16.	*N*/32.	*N*/64.
Volts	0·522	0·524	0·537	0·547	0·559	0·557	0·560	0·576	0·587

It will be seen that the variation of overvoltage with concentration of the sulphuric acid is only slight, but there is a distinct rise with decrease of concentration throughout. Part of this may possibly be due to concentration polarisation set up by local dilution of the electrolyte, particularly in the case of the very dilute electrolytes. The values given were obtained with stirring by means of a rapid current of hydrogen. The overvoltages obtained in other acid electrolytes are very close to those quoted. Thus, overvoltages in phosphoric acid are almost identical with those found for sulphuric acid of the same p_H, whereas overvoltages in hydrochloric and oxalic acids are about 2 centivolts higher. The overvoltage found for tartaric acid was distinctly abnormal. It first assumed a value about 5 centivolts below that of other acids, and after the cathode had been in the electrolyte for about 45 minutes a further decrease of 7 centivolts was observed. It was also noted that during electrolysis for a few minutes the cathode assumed a dark colour. Further, when the cathode was left standing in fresh tartaric acid solution over-night, a small amount of antimony went into solution. The abnormal behaviour of tartaric acid with regard to overvoltage should be considered in conjunction with the abnormally high yield of stibine obtained in this electrolyte (*vide infra*). The results obtained are in general agreement with those found by Glasstone for lead and mercury cathodes (J., 1924, **125**, 2414, 2416).

Acid Solutions containing Alkali Salts.—Solutions of the following acids containing also their sodium salts were studied: Sulphuric, hydrochloric, phosphoric, and acetic. The original object of the experiments was to trace a connexion between the p_H value of the solution and the maximum (characteristic) overvoltage observed. For this purpose solutions of the pure acid were usually employed initially, and to these, successive quantities of sodium hydroxide solution were added. No simple results were obtained, however. The principal conclusions drawn were the following. (1) When the concentration of the alkali salt and the *C.D.* are not very high, overvoltage values are obtained which are either identical with, or only slightly higher than, those of pure acids having the same p_H value, and the appearance of the cathode is similar to what it would have been in the solution of the pure acid. Thus a *N*-solution of sulphuric acid gave a p_H voltage of 0·273 and an overvoltage of 0·538, whereas a similar solution which was also *N*/2 with respect to sodium sulphate gave a p_H voltage of 0·269, and an overvoltage of 0·559. On the other hand, when the quantity of acid was small relatively to that of the alkali, wholly different results were obtained. A very much higher *C.D.* and a longer time were required to establish the maximum overvoltage and the results were not so definite. The electrode appeared to be covered with a black deposit after an experiment, such as is met with when alkaline electrolytes are used. The final results were entirely different from those obtained with pure acid solutions of the same p_H. Thus a solution which was N with regard to sodium sulphate and approximately $N/25$ with regard to sulphuric acid required a *C.D.* of about 80 milliamps./sq. cm. to establish the maximum overvoltage of 1·245 volt. A solution containing only acid and having the same p_H voltage of 0·374 would have shown an overvoltage smaller by about 0·67 volt. Similarly, a solution which was approximately N with regard to phosphate and to which enough sodium hydroxide was added to give it a p_H voltage of 0·355 had not attained a constant overvoltage even for a *C.D.* of 140 milliamps./sq. cm. The overvoltage then was 0·85 volt as compared with 0·57 volt for a sulphuric acid solution of similar p_H value. Results of this kind were obtained whether the porous diaphragm or the bottle apparatus was used. They point to considerable concentration changes in the boundary layer at the electrode.

Yields of Stibine.—A lengthy series of experiments on yields of stibine in acid solution showed that stibine is formed only with great difficulty and in small yield. A scarcely perceptible unsteadiness in overvoltage is the only indication of the evolution of the gas. Experiments were carried out in which antimony cathodes were employed in solutions of sulphuric, hydrochloric, and tartaric acids. Further, both antimony and lead cathodes were used in solutions of the same acids to which antimonious or antimonic compounds had been added. Direct, intermittent, and alternating currents were used. The last named consisted of alternating pulses of direct current obtained by means of a rotating commutator from a continuous current supply, the strength of the pulses in either direction being capable of independent adjustment and measurement (J., 1926, 2971). The following is a brief survey of the results obtained, none of which confirmed those reported by Worrell (*loc. cit.*). No stibine was formed in N-sulphuric or hydrochloric acid with continuous current with *C.D.*'s up to about 100 milliamps./sq. cm. At a *C.D.* of 112 milliamps./sq. cm. an unweighable trace of the gas was detected. Smooth electrodes and electrodes roughened by previous electrolysis, both in acid alone and in acid containing antimony sulphate, were tried. The highest yield obtained in sulphuric acid solution was 0·25% with $16N$-acid and continuous current of 1600 milliamps./sq. cm. density. In hydrochloric acid, similar figures were obtained. When alternating current was employed in $4N$-hydrochloric acid, a *C.D.* of 30 millicoulombs/sec./sq. cm. when the working electrode was the cathode, and of 12 when it was the anode, sufficed to produce a yield of 0·3%. The yields obtained by continuous-current electrolysis of tartar emetic in tartaric acid solution were higher than those in other electrolytes. The electrode here becomes covered with a voluminous, black, spongy deposit. The highest yield obtained hitherto is 2·34%. This was found when a solution of *N*-tartaric acid was electrolysed with an alternating current of 7·8 milliamps./sq. cm. while the working electrode was the cathode, and of 2·9 while it was the anode. In general, it may be said that high *C.D.*'s are necessary for stibine formation. A limit is, however, soon reached in practice owing to heating of the electrolyte. Special experiments showed that when a hot electrolyte was used initially, no stibine was obtained in any circumstances. With both sulphuric and hydrochloric acids, a high concentration favours the formation of stibine, and results were given by very much lower *C.D.*'s with alternating than with direct current.

Results obtained in Alkaline Solution. (*Experiments by* J. Grant.)

In the experiments in alkaline solution, hydrogen was always bubbled through the liquid. It was found particularly necessary to do this when the direct method was employed in order to remove small bubbles from the mouth of the glass capillary leading to the hydrogen electrode. Considerably more time elapsed in these experiments before readings became constant than in those in acid solution. It varied in different cases from 5 to about 30 minutes, but the final results were repeatable. Overvoltages in the following solutions were studied: 8*N*-, *N*-, and *N*/10-Sodium hydroxide; *N*-sodium carbonate and -sodium hydrogen carbonate; half-saturated baryta, calcium hydroxide, and disodium hydrogen phosphate; *N*-ammonium hydroxide and -ammonium carbonate; approximately *N*/45- and *N*/19-tetramethylammonium hydroxide; *N*/37-tetraethylammonium hydroxide; and *N*-sodium sulphate. The temperature was in all cases about 20°.

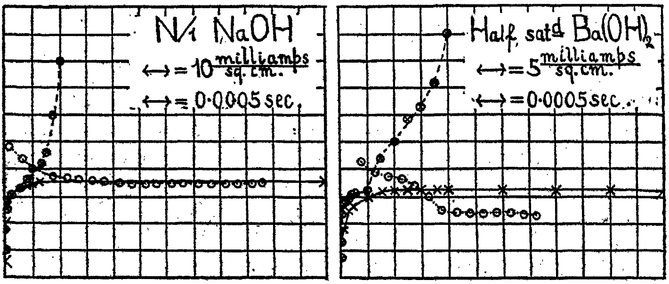
Table III gives overvoltages determined both by the direct and by the commutator method in solutions of *N*-sodium hydroxide and half-saturated baryta. These results may be taken as representative of those obtained in other solutions. Current densities are recorded in the first line in milliamps./sq. cm. under the heading *C.D.* (see p. 382). The overvoltages are assembled in the other lines, and are stated in millivolts. They are classified according to the solution and type of measurement—direct or commutator—as NaOH, *d*; NaOH, *c*; etc. The commutator employed for the latter gave average polarisations during the first 0·0137 sec. after breaking the current in the case of baryta, and in the case of the sodium hydroxide both 0·008 and 0·005 sec. were used without alteration of the results. It will be seen that, as in acid solution, the results obtained in a given electrolyte by the direct and commutator methods do not differ much for a given *C.D.* as long as this is small. The large divergences only occur at higher *C.D.*'s.

TABLE III.

C.D. ……	0·2	0·3	0·5	0·7	1·5	5·0	10·0	12·5	15	20	40	170
NaOH, *c*	390	420	455	525	550	635	690	710	715	715	715	715
NaOH, *d*	200	355	500	530	585	655	800	840	920	1600	—	—
$Ba(OH)_2$, *c*	115	190	325	350	495	595	635	635	635	635	635	635
$Ba(OH)_2$, *d*	135	255	455	535	590	640	995	1160	1250	1800	—	—

The decay of polarisation was also determined by means of the new commutator, the interval during which a measurement was made being 1/4000 sec. In Table IV, the mean times, t, of these intervals and the polarisations ω are given for N-sodium hydroxide and half-saturated baryta for *C.D.*'s well above the critical values. The results for other solutions are similar in nature.

FIG. 4.



×× -×-×- *Commutator method.* ⊗ ⊗ -⊗-⊗- *Direct method.*
○ ○ -⊖-⊖- *Decay curve.*

TABLE IV.

t (10^{-4} sec.).	1·25	3·75	6·25	8·75	11·25	13·75	16·25	18·75	21·25	23·75	26·25	28·75	31·25	33·75	36·25	38·75
ω NaOH	945	870	795	750	745	730	720	715	700	695	690	690	690	690	690	695
(Millivolts) $Ba(OH)_2$	—	845	780	755	740	675	600	500	480	470	475	480	475	470	450	—

The numbers recorded in Tables III and IV are plotted in Fig. 4. The full lines refer to results obtained by the commutator method, the broken lines to those found by the direct method; the abscissæ are current densities and the ordinates overvoltages. It will be seen (1) that, as is known, the commutator overvoltage in every case reaches a constant maximum; and (2) that at voltages not far removed from these maxima, the overvoltage–current density curve determined by the direct method shows a distinct inflexion or bend, which appears to indicate the setting in of some constant-voltage process absorbing considerable current and possibly of a chemical nature. The results of Table IV have been plotted into the diagram as dotted lines, and may be termed decay curves of polarisation; the abscissæ of these are times on the scale shown. It will be seen that the curves descend from a high polarisation value to one that remains nearly constant for a comparatively long time, and is not far removed from that indicated by the full curves. This again points to a large reserve of polarisation at certain voltages and indicates a chemical rather than a physical explanation. It may be connected with the formation of sodium alloys on the surface of the cathode.

Table V gives a summary of overpotentials found in alkaline solution. The overvoltages given under the heading ω_c in the second line were determined by means of one of the commutators; they are in most cases polarisations during the first 1/200 sec. after interrupting the current, some of them being averages of a number of determinations. On the line marked ω_d are assembled values of overvoltage which have been determined from the current density–overvoltage curves given by the direct method. These values are taken from the curves at positions as close as possible to where the inflexion occurs. The electrolytes are given in the order of decreasing p_H. It will be seen that, although there is a general increase of overvoltage with decreasing p_H, a number of the electrolytes examined fall out of line. There is thus no question of an accurate agreement with the relation previously proposed (J., 1924, **125**, 162), *viz.*, $\omega + 2h = c$, where ω is the overvoltage, h the *P.D.* between a standard electrode and the hydrogen electrode in the solution examined, and c a constant. The possibility cannot, however, be dismissed that we are dealing with a relation of the form proposed which is vitiated by secondary interfering influences. The matter is being further investigated also with electrodes other than antimony. Except in the case of sodium hydroxide solutions, there is no indication of any direct relation between sodium-ion concentration and overvoltage as was suggested by Herasymenko (*Rec. trav. chim.*, 1925, **44**, 503).

TABLE V.

Solution.	8*N*-NaOH.	*N*-NaOH.	$Ba(OH)_2$ (half-sat.).	*N*/10-NaOH.	*N*-NH_4OH.	$Ca(OH)_2$ (half-sat.).
ω_c (volt)	0·64	0·72	0·60	0·73	0·50	0·46
ω_d (volt)		0·70	0·65			0·90

Solution.	*N*-Na_2CO_3.	*N*/37-NEt_4OH.	*N*/90-NMe_4OH.	Na_2HPO_4 (half-sat.).	*N*-$NaHCO_3$.	*N*-Na_2SO_4.
ω_c (volt)	0·74	0·87	0·93	1·22	0·94	1·24
ω_d (volt)		0·95		1·20		1·27

Experiments on the Evolution of Stibine by Electrolysis in Sodium Hydroxide Solution.—Reference has already been made to the fact that in alkaline solution the antimony cathode becomes blackened during electrolysis. Some antimony is always found dissolved in the solution after the experiments. The black deposit is loose and may be rubbed off with a finger. It appears to have little effect on overvoltage results. It is different in character from deposits obtained under similar conditions on metals such as cadmium which form insoluble hydroxides in alkaline solution. As the *C.D.* is increased a precipitate begins to deposit in the electrolyte. The supposition previously made, that it is formed from stibine which is primarily evolved, has been proved correct as will be shown below. The precipitate appears to have all the properties of metallic antimony. Experiments were also carried out in which hydrogen containing stibine was generated from hydrochloric acid containing tartar emetic by means of zinc and then passed through 8*N*-sodium hydroxide. A precipitate forms very slowly and again appears to have all the properties of finely-divided metallic antimony. We can in no wise confirm the statement made by Weeks and Druce (*Rec. trav. chim.*, 1925, **44**, 971) that either of these precipitates has the properties ascribed by these authors to their hydride (J., 1925, **127**, 1069). The total quantity of antimony present in solution and as metal appears to increase continuously with *C.D.* for a given amount of current. Experiments were carried out, in the manner recorded previously, in which the hydrogen generated electrolytically on the antimony cathode was collected after drying and passing through absorption apparatus for stibine. Only at very high *C.D.*'s was blackening in the latter noted. In 8*N*-sodium hydroxide, the maximum yield of stibine gas amounted to 0·18% by volume for a *C.D.* of 150 milliamps./sq. cm. (intermittent). Experiments were also performed in which the amounts of antimony precipitated as metal by intermittent current of various densities, and also the amounts which had dissolved, were determined, the electrolyte being *N*- or 8*N*-sodium hydroxide. From these experiments, yields of stibine were calculated on the assumption that all the antimony found owed its presence to the primary production of this gas. The yields thus found varied between 0·32 and 1·71% by volume for *C.D.*'s varying between 15 and 150 milliamps./sq. cm. The lowest *C.D.* at which the antimony precipitated as metal was weighable was 35 milliamps./sq. cm. for *N*-, and .50 for 8*N*-sodium hydroxide. After metallic antimony has begun to form, the amount going into solution does not increase appreciably with increasing *C.D.* The experience gained from these experiments suggested the possibility that if hydrogen were blown rapidly past the working electrode it might carry the stibine with it before the latter had time to decompose. To test this, a small cone-shaped electrode was used, which pointed downwards towards the flared exit of a tube from which purified hydrogen was rapidly blown. The amount of hydrogen generated electrolytically was calculated from the current strength and time. The exposed area of the cathode varied in different experiments from 2 to 3·5 sq. cm. The results fully justified expectations, and prove that the antimony found distributed in the electrolyte has been formed from stibine primarily produced. The yields obtained in this way in *N*-sodium hydroxide are recorded in Table VI. It will be seen that the highest yield of stibine obtained as such amounted to 2%. It is noteworthy that with the very high *C.D.*'s the antimony cathode showed progressively less of the black deposit. The heating which occurs with high *C.D.* sets a limit to the yields. The experiments are being continued.

TABLE VI.

Type of current.	Millicoulombs per sq. cm.	Yield %.		
		As SbH_3.	Sb in pot.	Total.
Continuous	150	0·22	0·05	0·27
	250	0·21	0·26	0·47
	500	0·13	0·24	0·37
	1000	0·47	0·56	1·03
	2500	2·03	0·42	2·45
Intermittent	20	0·12	—	0·12
	50	0·32	0·22	0·54
	200	1·10	0·56	1·66
	370	1·50	2·00	3·50

Summary of Results and Conclusions.

1. In all cases examined, the current density–overvoltage curves obtained by the direct method bear a relation to those found under corresponding conditions by the commutator method.

2. It has been shown that in acid solution small polarisations maintain their value practically constant for periods up to 1/140 sec. At higher *C.D.*'s the polarisations fall off rapidly with time, but in all cases the polarisation measured during a given time-interval after the breaking of the current assumes a maximum value independent of the polarising current. Even when the interval during which the measurement is made is only 1/5000 sec. after the breaking of the current, such a maximum is obtained, and there is thus a discontinuity between it and the polarisation value shown by the direct method, the latter increasing indefinitely with *C.D.* This is in agreement with results obtained by means of the cathode-ray oscillograph by Newbery (*loc. cit.*) for other cathodes, but not with

the views propounded by Knobel (*loc. cit.*) on what appears to the authors to be insufficient experimental evidence.

3. In the best-conducting solutions, the increase of overvoltage found by the direct method becomes almost proportional to increase of *C.D.* for high values of the latter. This may be taken as evidence that overpotential measured by the direct method at high *C.D.*'s consists of the sum of a true polarisation, which is almost independent of the *C.D.*, and a term which results from passing the current through a more or less constant resistance at the surface of the electrode.

4. Replacing Gore's term "transfer-resistance" by the term "transfer-impedance," to describe effects of which the irreversibility or otherwise has not been established experimentally, our results may be described by saying that, in some of the cases examined, transfer-impedance has been proved to be irreversible after 1/5000 sec.

5. The time–polarisation curve shows considerable change in direction on extrapolating it backwards to zero time, and we therefore recommend that the polarisation measured and the time-interval of its measurement should be stated, rather than that attempts should be made to extrapolate to zero time from a small number of measurements as advocated by Glasstone (*loc. cit.*). We have confirmed in a number of cases that the values obtained sufficiently closely represent the average polarisation during the time of measurement and that they are not greatly affected by slight variations of the latter.

6. Overpotentials found in acid solution increase slightly with dilution. The effect is, however, smaller than corresponds to the relation $\omega - h = c$, in which the symbols have the significance attached to them above (p. 392). Experiments by Herasymenko (*loc. cit.*), for which the above relation holds, are therefore of a different character from ours.

7. Solutions containing relatively large amounts of alkali salts require high *C.D.*'s to establish constant overvoltages by the commutator method, and the results are similar in character to those obtained in alkaline solution. Here, doubtless, local changes of composition are operative. Where our results for antimony cathodes cover ground already explored for lead and mercury by Glasstone (*loc. cit.*), they are in general agreement with his.

8. No results of a general nature could be obtained connecting the production of stibine in acid solution with overpotential. The yields were small and appeared to depend largely on the solubility of the cathode in the electrolyte, and on extremely high values of *C.D.*

9. In alkaline solution, the overvoltage–current density curves obtained by the direct method show an arrest or inflexion which usually takes place at a voltage not far removed from the maximum given by the commutator method. The decay curves representing the overvoltage at successive short intervals after breaking the current also give indications of this same value, for they sink to, and become constant for a considerable time at, a potential not far removed from it.

10. The relation $\omega + 2h = c$, previously proposed by Sand and Weeks, could not be confirmed with any degree of accuracy, but the results suggest the probability that a relation of the kind may exist which is vitiated by secondary interfering influences.

11. The formation of stibine appears to proceed somewhat more readily in alkaline than in acid solution, and the conditions favourable to it are similar in the two cases. To obtain appreciable yields of the gas, however, it is necessary to blow a rapid current of hydrogen past the electrode, in order to carry away the nascent gas before it has been decomposed by the alkaline solution. The decomposition product formed, when this is not done, has the properties of metallic antimony.

We desire to express our indebtedness to the Chemical Society for a grant by means of which some of the materials used in this research were purchased.

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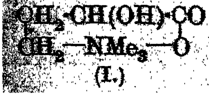
[*Received, October 22nd*, 1926.]

LIX.—*The Constitution of Carnitine. Part I. The Synthesis of α-Hydroxy-γ-butyrotrimethylbetaine.*

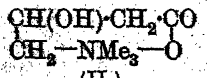
By JOHN WILLIAM CROOM CRAWFORD and JOSEPH KENYON.

IN spite of several investigations the constitution of carnitine, a constituent of muscular tissue, remains unsettled. Two formulæ (I and II) put forward by Krimberg (*Z. physiol. Chem.*, 1907, **53**, 525) represent carnitine as α(or β)-hydroxy-γ-butyrotrimethylbetaine, of which the latter was preferred because of the appearance of β-hydroxy-*n*-butyric acid in the animal organism (*ibid.*, 1908, **56**, 417). A third formula (III) was subsequently advanced by Engeland (*Ber.*, 1921, **54**, 2208) in which carnitine is represented as β′-hydroxy-β-*iso*butyrotrimethylbetaine.



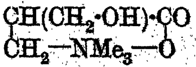
$$\begin{array}{l}CH_2\cdot CH(OH)\cdot CO\\ CH_2-NMe_3-O\end{array}$$

(I.)



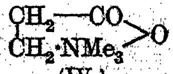
$$\begin{array}{l}CH(OH)\cdot CH_2\cdot CO\\ CH_2-NMe_3-O\end{array}$$

(II.)



$$\begin{array}{l}CH(CH_2\cdot OH)\cdot CO\\ CH_2-NMe_3-O\end{array}$$

(III.)



$$\begin{array}{l}CH_2-CO\\ CH_2\cdot NMe_3\end{array}>O$$

(IV.)

The evidence in support of (I) is that carnitine on oxidation with calcium permanganate yields β-homobetaine (IV) (Engeland, *Ber.*, 1909, **42**, 2457) and on distillation with aqueous baryta gives trimethylamine and crotonic and succinic acids: the production of these two acids is explained by the simultaneous oxidation and reduction of αγ-dihydroxy-*n*-butyric acid, which might be expected to be produced when trimethylamine is eliminated from the carnitine molecule. In favour of (II) is the fact that carnitine, when heated with sulphuric acid at 130°, loses a molecular proportion of water to yield an unsaturated betaine—"*apo*carnitine"—which is reduced by hydrogen in the presence of palladium to γ-butyrotrimethylbetaine (Engeland, *Ber.*, 1921, **54**, 2208). This point, however, does not appear to be well established, as the following data indicate. The reduction product of *apo*carnitine gave a chloroaurate, m. p. 201—203°. On the other hand, the synthetic γ-butyrotrimethylbetaine prepared by Willstätter's method (*Ber.*, 1902, **35**, 617) by Krimberg (*loc. cit.*) gave a chloroaurate of which the highest value of the m. p. was 182—184°.

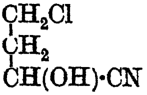
There does not appear to be any direct experimental evidence in favour of (III): it was advanced as an alternative when Engeland (*loc. cit.*) found that the α-hydroxy-γ-butyrotrimethylbetaine synthesised by the method of Fischer and Göddertz (*vide infra*) was unaffected by hot sulphuric acid under conditions which bring about the dehydration of carnitine.

Moreover, β-hydroxy-γ-butyrotrimethylbetaine has been synthesised by Rollett (*Z. physiol. Chem.*, 1910, **69**, 60), by Engeland (*Ber.*, 1910, **43**, 2705) and by Tomita (*Z. physiol. Chem.*, 1923, **124**, 253), and Engeland states that the properties of his synthetic betaine differed considerably from those of natural carnitine.

α-Hydroxy-γ-butyrotrimethylbetaine has been synthesised by Fischer and Göddertz (*Ber.*, 1910, **43**, 3278) as follows: α-Bromo-γ-phthalimido-*n*-butyric acid was heated with chalk and water, and the resulting hydroxy-derivative hydrolysed with hydrochloric acid to give γ-amino-α-hydroxy-*n*-butyric acid which, by treatment with alcoholic potassium hydroxide and methyl iodide, yielded α-hydroxy-γ-butyrotrimethylbetaine. The validity of this synthesis has been questioned by Engeland (*Ber.*, 1921, **54**, 2208) on the ground that it was shown by Berlin (*Z. Biol.*, 1907, **53**, 514) that, when phthal-β-bromo-*n*-propylimide is hydrolysed by the method described above, it yields, not only the expected β-aminopropyl alcohol, but also α-aminopropyl alcohol as the result of a molecular rearrangement.

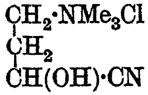
It was therefore decided to undertake the synthesis of α-hydroxy-γ-butyrotrimethylbetaine by an alternative method and to ascertain whether the properties of the product thus obtained agreed with those of (*a*) the synthetic betaine of Fischer and Göddertz, (*b*) natural carnitine.

The outline of the synthesis is as follows: β-Chloropropaldehyde diethylacetal, prepared by the action of alcoholic hydrogen chloride on acraldehyde, was hydrolysed by water, and the resulting β-chloropropaldehyde converted into its potassium bisulphite compound; the latter, by the action of potassium cyanide, gave *γ-chloro-α-hydroxy-*n*-butyronitrile* (V), which in turn gave, by the addition of trimethylamine, the *methochloride* of γ-dimethylamino-α-hydroxy-*n*-butyronitrile (VI). On hydrolysis with hydrochloric acid, this nitrile gave the *hydrochloride* of α-hydroxy-γ-butyrotrimethylbetaine (VII).



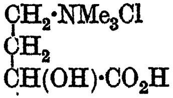
$$\begin{array}{l} CH_2Cl \\ | \\ CH_2 \\ | \\ CH(OH)\cdot CN \end{array}$$

(V.)



$$\begin{array}{l} CH_2\cdot NMe_3Cl \\ | \\ CH_2 \\ | \\ CH(OH)\cdot CN \end{array}$$

(VI.)



$$\begin{array}{l} CH_2\cdot NMe_3Cl \\ | \\ CH_2 \\ | \\ CH(OH)\cdot CO_2H \end{array}$$

(VII.)

The properties of the compound thus obtained agree with those given by Fischer and Göddertz for their synthetic betaine; there can be little doubt, therefore, that the betaine obtained by these authors and that described in this communication are both α-hydroxy-γ-butyrotrimethylbetaine, and that, in consequence, the doubts of Engeland are not justified.

Although Fischer and Göddertz (*loc. cit.*) state that the m. p.'s of several derivatives of their synthetic betaine differ considerably from those of corresponding derivatives of natural *l*-carnitine [according to Kutscher (private communication to Engeland, *Ber.*, 1921, **54**, 2208), carnitine can be racemised by a method which was not described, and the chloroaurate of the racemised compound has the same melting point as that of the chloroaurate of the optically active base], it was decided to attempt the resolution of the synthetic α-hydroxy-γ-butyrotrimethylbetaine in order to prepare crystalline derivatives of its optically active modifications, but unfortunately the attempt was not successful. This drawback is, however, not so serious as was at first thought, since it was found that, contrary to the statement of Engeland (*loc. cit.*), the synthetic α-hydroxy-γ-butyrotrimethylbetaine is decomposed by sulphuric acid at temperatures up to 130° with the production of carbon monoxide—a behaviour quite different from that of carnitine with the same reagent. It is thus definitely established that carnitine cannot be α-hydroxy-γ-butyrotrimethylbetaine.

It is hoped to describe in a further communication the synthesis of β′-hydroxy-β-*iso*butyrotrimethylbetaine.

EXPERIMENTAL.

Large quantities of acraldehyde were readily prepared by Moureu's method (*Ann. Chim.*, 1921, **15**, 158).

The method of preparing β-chloropropaldehyde diethylacetal described by Wohl and Emmerich (*Ber.*, 1898, **31**, 1797; 1900, **33**, 2761) having given only about 17% of purified material, the following procedure, which was found after many trials to give the best results, was adopted. Dry hydrogen chloride was passed into a mechanically stirred solution of dry calcium chloride (400 g.) and acraldehyde (1000 g.) in 96% alcohol (2000 g.) at such a rate that saturation was reached in 8—10 hours, the reaction mixture being protected from moisture and being kept cold by means of ice. During the addition of hydrogen chloride, the separation of crystalline hydrated calcium chloride was continuous. Next day the liquid portion, consisting of a small upper layer of aqueous-alcoholic calcium chloride solution superimposed on the crude acetal, was filtered or decanted from the solid calcium chloride, and the latter was washed with ether, which was then added to the liquid portion. This was neutralised by adding it drop by drop to a slight excess of cold, well-agitated 10% sodium hydroxide solution. The lime which had separated during the neutralisation was dissolved by the cautious addition of acetic acid, after which the layer of acetal separated quite readily. The aqueous layer was removed, and the acetal was washed with water, then with very dilute sodium hydroxide solution to render it alkaline once more, and finally with water. After drying with calcium chloride, 1653 g. of acetal, b. p. 72—76°/20 mm., were obtained. Yield 56·4%. On redistillation, the product came over almost completely at 74°/20 mm. and had $d_{4^\circ}^{18\cdot7^\circ}$ 0·9951, $d_{4^\circ}^{22\cdot3^\circ}$ 0·9845, $n_{\mathrm{D}}^{18\cdot7^\circ}$ 1·4206, $n_{\mathrm{D}}^{22\cdot3^\circ}$ 1·4203; $[R_L]_{\mathrm{D}}^{18\cdot7^\circ}$ 42·31, $[R_L]_{\mathrm{D}}^{22\cdot3^\circ}$ 42·84 (calc., 42·58).

When the dry hydrogen chloride was passed more rapidly (during 3—4 hours) into the solution, the yield of acetal fell to 48%.

The *potassium bisulphite compound of β-chloropropaldehyde* was prepared by heating under reflux on a water-bath a mixture of β-chloropropaldehyde diethylacetal (666 g.) and water (72 g.; 2 mols.), with frequent shaking until reaction set in; this became apparent by the coalescence of the two liquid layers and the simultaneous refluxing of alcohol. The quickly cooled reaction liquid was vigorously shaken with a concentrated solution of potassium bisulphite (1·1 mols.), the mixture separated, and the unhydrolysed acetal (about 450 g.) reheated with water. This procedure was repeated four times; the amount of unhydrolysed acetal then amounted to only about 5 g. The potassium bisulphite compound was precipitated in soft, white crystals on addition of alcohol (Found : K, 18·4. Calc. : K, 18·4%). The corresponding sodium bisulphite compound forms nacreous plates (Found : Na, 11·8. Calc. : Na, 11·7%). For the preparation of γ-chloro-α-hydroxy-*n*-butyronitrile, however, it is unnecessary to isolate the solid bisulphite compound : the solution was used direct.

*γ-Chloro-α-hydroxy-*n*-butyronitrile* (V) was prepared by adding during ½ hour a cold aqueous solution of potassium cyanide (400 g. of 92%) to a well-stirred solution of the bisulphite compound, kept below 20°. The upper layer of nitrile was separated, the aqueous portion extracted with ether, and the mixture of nitrile and ethereal extract washed with very dilute acid, dried with sodium sulphate and distilled. The *nitrile* distilled at 91·5°/3 mm. (yield, 316 g.; 66%). It is a colourless, odourless, slightly viscous liquid which can be distilled only at low pressures; $d_{4^\circ}^{19\cdot1^\circ}$ 1·0795, $d_{4^\circ}^{23\cdot1^\circ}$ 1·0765, $n_D^{19\cdot1^\circ}$ 1·4399, $n_D^{23\cdot1^\circ}$ 1·4387 (Found : N, 11·7. C_4H_6ONCl requires N, 11·7%).

γ-Chloro-α-cyanopropyl benzoate, prepared by the interaction of γ-chloro-α-hydroxy-*n*-butyronitrile (24 g.), pyridine (17 g.), and benzoyl chloride (29 g.) in ethereal solution, distilled at 147°/3—4 mm. to give a colourless, viscous, highly refractive liquid which soon solidified (yield, 35 g.; 82%). Recrystallised from light petroleum (400 c.c.), it formed small, soft needles, m. p. 59° (Found : N, 6·4. $C_{11}H_{10}O_2NCl$ requires N, 6·3%). The *acetate,* obtained in a similar manner or by the action of boiling acetic anhydride (1 mol.), has b. p. 116—117°/11 mm. and is an odourless, fairly mobile liquid heavier than water; $n_{5790}^{20\cdot1^\circ}$ 1·4342, $n_{5461}^{20\cdot1^\circ}$ 1·4355, $n_{4359}^{20\cdot1^\circ}$ 1·4433 (Found : N, 8·8. $C_6H_8O_2NCl$ requires N, 8·7%).

*γ-Dimethylamino-α-hydroxy-*n*-butyronitrile Methochloride* (VI).— γ-Chloro-α-hydroxy-*n*-butyronitrile (100 g.) was added to a well-stirred solution of trimethylamine (55 g.) in dry amyl alcohol (200 g.), and the mixture maintained at 35—40°; fine crystals of the *amino-nitrile methochloride* were rapidly deposited. After being stirred for several hours, the mixture was cooled and filtered, and the crystalline material washed with dry ether : the amyl alcohol–ether filtrate deposited a second crop of the methochloride, which was removed and washed. Some uncombined γ-chloro-α-hydroxy-*n*-butyronitrile was recovered after the amyl-alcoholic filtrate had been washed with dilute hydrochloric acid to remove trimethylamine and distilled in a vacuum. The methochloride (yield 75—85%) was recrystallised from amyl alcohol (temperature not above 95°) or precipitated from its solution in absolute alcohol by addition of dry ether and was thus obtained in small, glistening, transparent, very hygroscopic plates, m. p. 137°. It is insoluble in chloroform, benzene, ether, or acetone (Found: N, 15·6. $C_7H_{15}ON_2Cl$ requires N, 15·6%).

The *chloroaurate*, prepared in the usual manner, crystallised, on slow cooling of its aqueous solution, in long, hairy, yellow needles, m. p. 95° (Found: Au, 40·9. $C_7H_{15}ON_2Cl_4Au$ requires Au, 40·9%). The *chloroplatinate* crystallises from aqueous alcohol in radiating clusters of short, slender, orange needles, m. p. 239—240° (decomp.) (Found: Pt, 28·2. $C_{14}H_{30}O_2N_4Cl_6Pt$ requires Pt, 28·1%).

α-Hydroxy-γ-butyrotrimethylbetaine Hydrochloride (VII).—A mixture of γ-dimethylamino-α-hydroxy-*n*-butyronitrile methochloride (225 g.), water (270 c.c.), and hydrochloric acid (270 c.c.; 2 mols.) was gently boiled for 2 hours, water being added from time to time to keep the volume of the solution constant. The solution was then evaporated until of syrupy consistency and dried in a vacuum until completely solid. The dry material was heated under reflux with alcoholic hydrogen chloride (275 g. of 10%) for 4 hours. After 12 hours, the ammonium chloride was filtered off and washed with a little absolute alcohol, and the combined filtrate and washings were mixed with an equal volume of water and distilled until the temperature was 95°. The residue was diluted with water, and the solution thus obtained was boiled with charcoal and evaporated until crystallisation set in; the crystalline material was filtered off, and the filtrate again evaporated. The process was repeated several times, the total yield of dry hydrochloride being 234 g. (94%). The betaine hydrochloride crystallises from alcohol in glistening prisms which are not excessively soluble in water, from which it may be crystallised—in marked contrast to the difficultly crystallisable *l*-carnitine hydrochloride.

The chloroaurate produced on mixing concentrated aqueous solutions of the betaine hydrochloride and gold chloride was twice recrystallised from water containing a trace of hydrochloric acid, from which it separated in orange-yellow crystals which, after drying at 105°, melted sharply at 173° without decomposition to give a deep orange-red liquid (Found: Au, 39·3; C, 16·6; H, 4·1; N, 2·9. Calc. for $C_7H_{16}O_3NCl_4Au$: Au, 39·3; C, 16·8; H, 3·2; N, 2·8%). The melting point was unaltered by further recrystallisation of the material. Fischer and Göddertz (*loc. cit.*) give m. p. 175—176° (corr.) after sintering. Carnitine chloroaurate has m. p. 153—154°.

A *chloroplatinate* was obtained by mixing equivalent quantities of the betaine hydrochloride and chloroplatinic acid in aqueous solution, evaporating the mixture to a syrupy consistency, and adding warm alcohol until the turbidity thus produced was permanent. On cooling, a small amount of oil, which rapidly solidified, separated along with orange, crystalline plates. These, after recrystallisation from aqueous alcohol, had m. p. 218° (decomp.) after softening at about 196° (Found: Pt, 24·8. $C_{18}H_{40}O_6N_2Cl_6Pt$ requires Pt, 24·75%). The compound is therefore most probably the chloroplatinate of the ethyl ester of α-hydroxy-γ-butyrotrimethylbetaine produced by the action of ethyl alcohol on the free acid.

By the addition of more alcohol to the filtrate, fine, slender, orange needles were obtained. These began to sinter at about 196° and melted at 210—212° (decomp.) (Found: Pt, 26·3. Calc. for $C_{14}H_{32}O_6N_2Cl_6Pt$: Pt, 26·6%). Fischer and Göddertz (*loc. cit.*) state that the compound prepared by them melts not quite constantly at 216° (corr.) after previous pronounced sintering. They do not, however, give any analytical data. Carnitine chloroplatinate has m. p. 214—218° (decomp.).

In an attempt to effect the resolution of α-hydroxy-γ-butyrotrimethylbetaine the *d*-bromocamphorsulphonate was prepared, but it was a gum which could not be crystallised. The d-*camphorsulphonate* of α-hydroxy-γ-butyrotrimethylbetaine was prepared as follows: The betaine hydrochloride (19·75 g.) and the calculated quantity of the silver salt of Reychler's *d*-camphorsulphonic acid were mixed in aqueous solution, the precipitated silver chloride was removed, the filtrate evaporated, and the resulting syrup kept in a vacuum over sulphuric acid for 2 months. The white, crystalline material obtained separated readily from acetone in tufts of small, slender needles. Repeated crystallisation, however, brought about no alteration in the original rotatory power of the salt.

One of the authors wishes to express his thanks for a grant from the Advisory Council of the Department of Scientific and Industrial Research.

BATTERSEA POLYTECHNIC. [*Received, November 22nd*, 1926.]

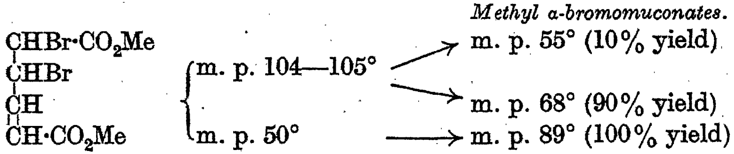
LX.—*Muconic and Hydromuconic Acids. Part IV. Geometrical Form and Reducibility.*

By ERNEST HAROLD FARMER and WALTER MARK DUFFIN.

GEOMETRICAL isomerides of the muconic acid series possess a considerable degree of permanency and can be kept in the light and enter into reaction without change of geometrical form (J., 1923, 123, 2531). The effect of geometrical form on certain types of molecular reactivity can readily be observed, therefore, and comparison be made with the behaviour of simple ethylenic compounds. In studying the hydrogenation process, twelve compounds of the muconic acid series have been submitted to reduction and every effort has been made to trace variation from the standard type of reduction product.

I. *Monohalogenated Muconic Esters.*

When *trans-trans*-methyl muconate is treated with bromine, two stereoisomeric bromides (I) are obtained; both of these forms revert to the parent substance on treatment with zinc. On treatment with organic bases, however, each isomeride behaves differently and three monobromomuconic esters are obtained according to the scheme:

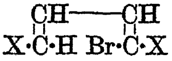


$$\begin{array}{l} CHBr{\cdot}CO_2Me \\ | \\ CHBr \\ | \\ CH \\ \| \\ CH{\cdot}CO_2Me \end{array}$$

(I.)

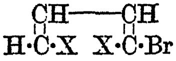
Careful search for the remaining one of the four theoretically possible isomerides (II), (III), (IV), and (V), in large quantities of material, proved fruitless. Although both the parent dibromides are *racemic* forms, the more fusible (corresponding to the racemic forms in the substituted succinic acids) might be expected to yield the less fusible (*trans-trans-*) methyl bromomuconate, and the less fusible (corresponding to a *meso*-form), the more fusible (geometrically inverted) form of methyl bromomuconate. In the absence of an absolute method of determining geometrical form, use has been made of their capacity for amide formation—a method typical of those used in observing steric effects. If, in the ester–amide transformation, activation preliminary to amide formation be assumed, it would appear to be restricted to the carbalkyloxy-groups acting as self-contained systems; otherwise, according to current conceptions of the activation process in unsaturated chains, the distinction between geometrical forms must disappear.

Each isomeride yielded an amide, two of the forms readily and without degradation, and the third with much greater difficulty and gross decomposition. Derivation, speed of amide formation and solubility being taken into account, the three isomeric methyl α-bromomuconates would seem to be capable of classification as below; since, however, in considering the main product of bromine addition to *trans-trans*-methyl muconate the method of geometrical inversion employed leads to more than one form, of which that regarded as *cis-cis* predominates, it is evident that molecular disturbance has gone too far to allow of the assumption that the *cis-trans*-form produced is necessarily that isomeride (IV) arising by simple inversion at one double bond.



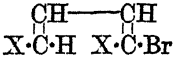
$$\begin{array}{cc}\mathrm{CH} & \mathrm{CH} \\ \mathrm{X\cdot C\cdot H} & \mathrm{Br\cdot C\cdot X}\end{array}$$

trans-trans
m. p. 89°
(II.)



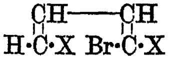
$$\begin{array}{cc}\mathrm{CH} & \mathrm{CH} \\ \mathrm{H\cdot C\cdot X} & \mathrm{X\cdot C\cdot Br}\end{array}$$

cis-cis
m. p. 68°
(III.)



$$\begin{array}{cc}\mathrm{CH} & \mathrm{CH} \\ \mathrm{X\cdot C\cdot H} & \mathrm{X\cdot C\cdot Br}\end{array}$$

cis-trans
m. p. 55°
(IV.)



$$\begin{array}{cc}\mathrm{CH} & \mathrm{CH} \\ \mathrm{H\cdot C\cdot X} & \mathrm{Br\cdot C\cdot X}\end{array}$$

cis-trans
(V.)

$X = CO_2Me$

Towards reducing agents, the three isomerides behave very differently. The *trans-trans*-form is reduced, on heating for a few minutes with zinc and alcohol, to *trans-trans*-methyl muconate and with zinc and acetic acid to methyl Δ^{β}-dihydromuconate. The *cis-cis*-form remains unreduced after prolonged treatment with these reagents, whilst the *cis-trans*-form readily gives an almost quantitative yield of methyl Δ^{β}-dihydromuconate after short heating with zinc and acetic acid, although it is not reduced by zinc and alcohol.

If it be taken that the oxygen of the carboxyl group plays an important part in the reduction of such unsaturated compounds, the experimental results are such as might have been expected to arise from the purely steric effect of the geometrical configuration : indeed it would seem that reduction is governed by the accessibility of the carboxyl group. It would appear probable, therefore, that the *cis-trans*-form (IV) was the one actually obtained and investigated and that the alternative form (V), if obtained, would be reducible to methyl muconate by zinc and alcohol.

II. *Dihalogenated Muconic Esters.*

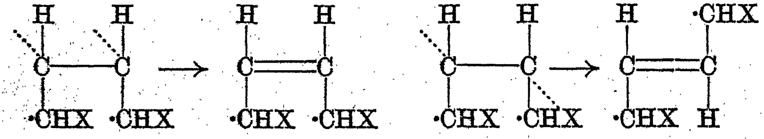
In this series, the three geometrical forms of ethyl $\alpha\alpha'$-dibromomuconate (*loc. cit.*) have been submitted to reduction. Each of the isomerides was reduced by zinc and acetic acid with such vigour and completeness that discrimination between the isomerides as to reducibility was impossible; the product in each case was ethyl dihydromuconate. A similar result was obtained with the two known forms of ethyl $\alpha\alpha'$-dichloromuconate (*loc. cit.*, p. 2544). There was the interesting result, however, that none of the three dibromo-esters was readily reduced (bromine replaced by hydrogen) with zinc and alcohol. Such a variation from the mode of reactivity of the monobromo-esters probably reflects the difference between a balanced and an unbalanced molecule.

III. *Muconic Esters.*

Reduction of *trans-trans*- and *cis-cis*-methyl muconate proceeds so slowly with reagents such as zinc and acetic acid that discrimination between their reducibility is impossible. With palladium and hydrogen, both forms are reduced to methyl adipate.

In all the preceding reductions the dihydrogenated product has been of one form (presumably *trans*-) entirely. Thus, almost quantitative yields of ethyl dihydromuconate (m. p. 2°) and methyl dihydromuconate (m. p. 16°) have been obtained repeatedly; no trace of a second form has been recognisable on any occasion. Since numerous attempts to isolate a second geometrical form, including the removal of bromine from the stereoisomeric methyl and ethyl $\beta\beta'$-dibromoadipates, have been unsuccessful, it appears certain that such a form can only have a very low degree of stability or is incapable of existence.

There appears no very obvious relationship between the geometrical form of the system $C{:}C{\cdot}C{:}C$ and that of its reduction product $CH{\cdot}C{:}C{\cdot}CH$; this is the case whether the process be represented on the Thiele, the Lowry, or the electronic plan. If represented in the van 't Hoff manner, reduction could yield *cis*- and *trans*-isomerides only by variation in the linking of the free valencies. Thus the two ways (A) and (B) are possible. Where *cis*- and *trans*-forms are of comparable stability, both isomerides might be expected to arise in the reduction of any one of the isomeric muconic forms. Departure from this equal favouring of *cis*- and *trans*-dispositions (subject to subsequent inversion processes due to experimental conditions) might arise (*a*) by the steric effects of the terminal groups tending towards *trans*-forms, and (*b*) by a tendency towards symmetrical disposition of free valencies as in (B) above, also tending to the production of *trans*-forms. If the effect of terminal addition is gained merely by the occurrence of a secondary effect, a process of molecular rearrangement, then the tendency (probably largely steric) towards stability might be expected to result in the appearance of *trans*-forms. The persistent occurrence of a single form of dihydromuconic ester in the foregoing reductions would seem to be the logical result, were it not for the failure of methods other than reduction to yield the geometrical isomeride. In extending observations to other muconic systems, an instance was discovered in which the form of the reduction product was dependent on that of the parent compound.



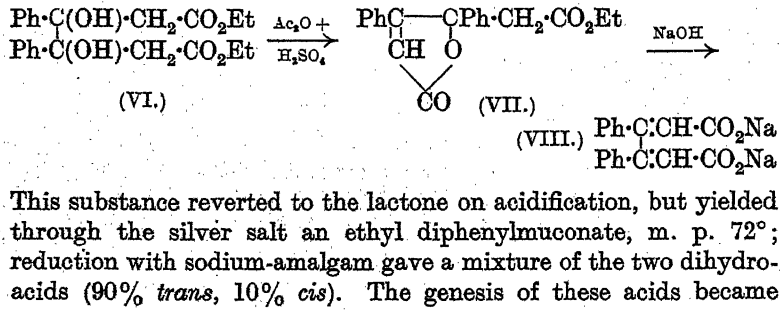
(A.) (B.)

IV. ββ'-*Diphenylmuconic Esters.*

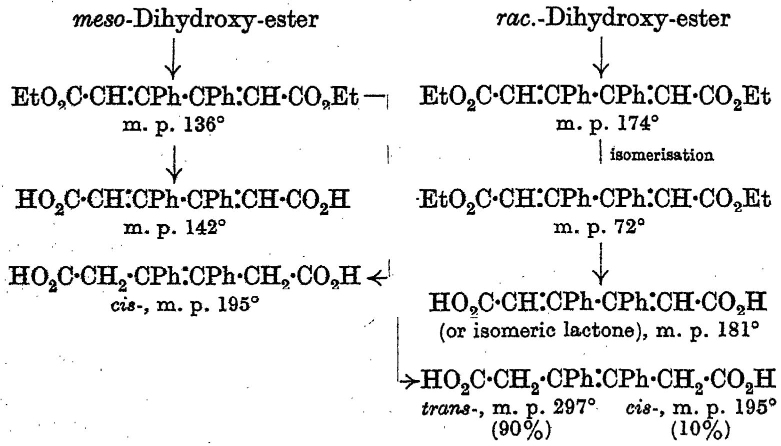
From ethyl *meso*-ββ'-diphenyl-ββ'-dihydroxyadipate Beschke (*Annalen*, 1912, **384**, 143) obtained two diphenyldihydromuconic acids related either as *cis*- and *trans*- or as Δ^{α}- and Δ^{β}-isomerides. On re-examination, Beschke's acids proved to be *cis*- and *trans*-forms of the Δ^{β}-acid; both yielded benzoylacetic acid as the sole isolable oxidation product when treated with ozone in alkaline solution:

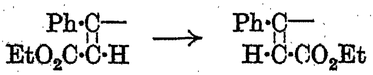
$$HO_2C{\cdot}CH_2{\cdot}CPh{:}CPh{\cdot}CH_2{\cdot}CO_2H \xrightarrow{O_3} 2COPh{\cdot}CH_2{\cdot}CO_2H.$$

The higher-melting acid has the *trans*-configuration, since Beschke showed that this form only could be converted into dihydroxychrysene. In Beschke's synthesis a sodium diphenylmuconate (VIII) was obtained from the dehydration product (VII) of the *meso*-dihydroxy-ester (VI).



This substance reverted to the lactone on acidification, but yielded through the silver salt an ethyl diphenylmuconate, m. p. 72°; reduction with sodium-amalgam gave a mixture of the two dihydro-acids (90% *trans*, 10% *cis*). The genesis of these acids became clearer when both dihydroxy-esters were submitted to dehydration under mild conditions. The two stereoisomerides then yielded different forms of ethyl diphenylmuconate, of which that derived from the *racemic* ester passed spontaneously, on short standing, into a third isomeride which proved to be identical with Beschke's ester. The production of the last from a *meso*-compound must have involved stereoisomeric inversion, due to the somewhat drastic conditions employed. Each of the stable esters yielded a corresponding acid on hydrolysis with sulphuric acid; each gave a characteristic product on reduction with sodium amalgam. Isomeric change of the unstable form was too rapid to allow of its reduction product being differentiated from those of its isomerides. It is impossible from the evidence obtained to assign formulæ to the three ethyl diphenylmuconates produced. All attempts to discover their individual configurations by oxidative processes (compare Behrend and Heyer, *Annalen*, 1919, **418**, 294) were unsuccessful owing to their great resistance to oxidation. It is quite clear, however, that the form of the reduction product has a definite relation to that of the parent butadiene compound; whether this is a necessary and fundamental result of the mechanism of reduction or merely a peculiarity arising from the nature of the substituent groups in these substances can only be determined by an examination of other examples. A pronounced steric effect capable of deciding the configuration of the reduction product might be expected to lead to the formation of the same stable reduced form from all the isomeric butadiene esters, not to different forms of comparable stability. On the other hand, it is probable that the spontaneous isomerisation noted above is a volume effect of the kind


meso-Dihydroxy-ester
$EtO_2C·CH:CPh·CPh:CH·CO_2Et$
m. p. 136°
$HO_2C·CH:CPh·CPh:CH·CO_2H$
m. p. 142°
$HO_2C·CH_2·CPh:CPh·CH_2·CO_2H$
cis-, m. p. 195°
rac.-Dihydroxy-ester
$EtO_2C·CH:CPh·CPh:CH·CO_2Et$
m. p. 174°
isomerisation
$EtO_2C·CH:CPh·CPh:CH·CO_2Et$
m. p. 72°
$HO_2C·CH:CPh·CPh:CH·CO_2H$
(or isomeric lactone), m. p. 181°
$HO_2C·CH_2·CPh:CPh·CH_2·CO_2H$
trans-, m. p. 297° *cis*-, m. p. 195°
(90%) (10%)



$$\begin{matrix} Ph·C— \\ \parallel \\ EtO_2C·C·H \end{matrix} \longrightarrow \begin{matrix} Ph·C— \\ \parallel \\ H·C·CO_2Et \end{matrix}$$

rather than the reverse.

EXPERIMENTAL.

Methyl Muconate Dibromide.—The gradual addition of bromine (1 mol.) to *trans-trans*-methyl muconate in chloroform solution in direct sunlight gave a product, isolated by evaporation of the solvent in a vacuum, consisting of two isomeric *dibromides* in the approximate proportion 12 : 1, which were separated by fractional crystallisation from ethyl alcohol or petroleum (b. p. 60—80°). The less soluble, more abundant form crystallised in stout, colourless prisms, m. p. 104—105° (Found : Br, 48·35. $C_8H_{10}O_4Br_2$ requires Br, 48·4%), the more soluble form as a coarse powder, m. p. 50° (Found : Br, 48·4%).

Isomeric Methyl α-Bromomuconates.—Dry ethereal solutions of the isomeric dibromides were treated in turn with ethereal diethylamine in slight excess. Diethylamine hydrobromide separated rapidly and quantitatively in each case. The ethereal solutions, freed from base by washing with dilute acid, yielded, on evaporation, colourless oils which solidified completely. The product from the more fusible dibromide was homogeneous; it crystallised from ethyl alcohol or petroleum in long, stout needles, m. p. 89° (Found : Br, 31·95. $C_8H_9O_4Br$ requires Br, 32·1%).

The less fusible dibromide yielded a mixture of isomeric monobromo-esters. These were separated completely only by a prolonged and laborious process of fractional crystallisation, using ethyl alcohol and petroleum (b. p. 60—80°) alternately. The less soluble of these isomerides crystallised from alcohol or petroleum in stout prisms, m. p. 68° (Found : Br, 32·1%); the more soluble crystallised from alcohol in small, compact prisms, m. p. 55° (Found: Br, 31·9%). It is a remarkable fact that, although these isomerides were stable when pure, mixtures of the two lower-melting forms invariably changed in a few days to a viscous, pale yellow oil, no longer crystallisable. Removal of hydrogen bromide from the two methyl muconate dibromides could also be accomplished by the use of excess of hot pyridine or the calculated quantity of cold alcoholic sodium methoxide.

Formation of Amides from Isomeric Methyl α-Bromomuconates.—Equal quantities of the three isomerides were treated with excess of concentrated aqueous ammonia at room temperature. The esters gradually dissolved, with the separation of crystalline amides. The approximate times of conversion are shown in the table below :

Bromo-ester. M. p.	Suggested form.	Comparative solubility in organic solvents.	Time of conversion into amide.	Amide. M. p.
89°	*trans-trans*	Most insoluble	4 hours (no decomp.)	235°
68	*cis-cis*		9 hours (gross decomp.)	197
55	*cis-trans*	Most soluble	2½ hours (no decomp.)	156

The *trans-trans*-amide (m. p. 235°) crystallised from water as a colourless powder (Found : Br, 36·5. $C_6H_7O_2N_2Br$ requires Br, 36·5%); the *cis-cis* (m. p. 197°) in stout prisms (Found : Br, 36·4%); the *cis-trans* in long needles (Found : Br, 36·6%).

Reduction of Methyl α-Bromomuconates.—(a) *With zinc and acetic acid.* To the ester, dissolved in glacial acetic acid, excess of zinc dust was added in small quantities. The mixture was heated on a steam-bath for 20 minutes, cooled, poured into water, and filtered. The ethereal extract of the filtrate was freed from acetic acid and dried, and the solvent evaporated.

The *trans-trans*-ester was readily reduced: the product, which solidified on cooling, crystallised from light petroleum in well-formed, colourless prisms, m. p. 16°, which obviously represented only one of the two possible geometrical forms of *methyl* Δ^{β}-*dihydromuconate* (Found: C, 55·7; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). Only the slightest trace of non-crystallisable ester remained in the solvent. Bromination of this ester in chloroform solution gave an almost quantitative yield of the methyl ββ′-dibromoadipate, m. p. 93° (*loc. cit.*, p. 2541). Hydrolysis with dilute sulphuric acid yielded pure Δ^{β}-dihydromuconic acid.

The reduction of the *cis-cis*-ester was attempted in a similar fashion. The product after 20 minutes' heating was an oil which did not solidify. On distillation, it was obtained as a colourless oil of boiling point and composition differing little from those of the original compound. Further treatment with zinc and acetic acid for 1 hour yielded a similar oil with a large bromine content. Inability to crystallise these products probably arose from admixture of slight quantities of reduction products; it was frequently found that mixtures of the isomeric bromo-esters with small amounts of impurities could be solidified only with the utmost difficulty.

Reduction of the *cis-trans*-ester to methyl Δ^{β}-dihydromuconate, m. p. 16°, proceeded exactly as with the *trans-trans*-form. In this case also, only one geometrical form of the reduced product could be isolated.

(b) *Zinc and alcohol* (*or acetone*). The *trans-trans*-monobromo-ester was refluxed with acetone and excess of zinc dust. Crystals of *trans-trans*-methyl muconate soon separated from the boiling solution. After ½ hour the suspended methyl muconate was redissolved by addition of more acetone, and the resulting solution filtered. The filtrate gave, on evaporation, an almost quantitative yield of methyl muconate, which crystallised from methyl alcohol in the characteristic, long needles, m. p. 156°.

The *cis-cis*-ester was treated similarly, but was recovered unchanged. The bulk of the *cis-trans*-ester was recovered in pure condition after treatment in this way: if any reduction occurred, it was insignificant in extent.

Reduction of Isomeric Ethyl αα′-*Dibromomuconates*.—These substances were prepared as described in Part II of this series (*loc. cit.*). Each of the three isomerides passed almost quantitatively into ethyl dihydromuconate on treatment with zinc and acetic acid as above. A careful examination of the reduction product was made in each case. Hydrolysis with dilute sulphuric acid yielded only Δ^{β}-dihydromuconic acid, m. p. 197°, and recrystallisation from light petroleum yielded pure *ethyl* Δ^{β}-*dihydromuconate* (presumably *trans*-) in colourless prisms, m. p. 2° (approx.). From the mother-liquor, only a very small quantity of non-crystallisable ester was obtained. This, on hydrolysis, also yielded dihydromuconic acid, m. p. 197°.

With zinc dust and alcohol (or acetone), no appreciable reduction was effected in ½ hour. Each of the three isomerides was recovered practically quantitatively.

Reduction of Isomeric Ethyl αα′-Dichloromuconates.—The two known isomerides (*loc. cit.*, p. 2540) were similarly treated with zinc dust and acetic acid. Rapid and complete reduction to ethyl Δ^{β}-dihydromuconate was effected. Again, only one form (m. p. 2° approx.) of this substance could be isolated.

Reduction of Isomeric Methyl Muconates.—(a) *With zinc and acetic acid.* Reduction of the two known isomerides (*loc. cit.*, p. 2546) proceeded so slowly with zinc and acetic acid that isomerisation of the lower-melting form probably preceded reduction. The product in each case was methyl Δ^{β}-dihydromuconate, m. p. 16°, or the corresponding acid.

(b) *With sodium amalgam.* The reduction of the *trans-trans*-acid (corresponding to the methyl ester, m. p. 156°) has previously been described. The product is entirely Δ^{β}-dihydromuconic acid, m. p. 197°. Methyl muconate, m. p. 75°, was hydrolysed with alkali to a mixture of the corresponding acid and lactone (*loc. cit.*, p. 2548), which was reduced in the usual way with sodium amalgam in a current of carbon dioxide. The product yielded ββ′-dihydromuconic acid, m. p. 197°, only.

(c) *With palladium and hydrogen.* The two isomerides yielded methyl adipate when reduced at atmospheric pressure by the method of Skita. Reduction to the dihydro-stage could not be secured by restricting the hydrogen supplied: in this case a portion of the ester remained unreduced.

Action of Zinc on Isomeric Methyl αα′-Dibromoadipates.—The two dibromo-esters (*loc. cit.*, p. 2541) were each dissolved in acetone and carefully treated with excess of zinc dust. Reaction, which took place rapidly, was completed by heating for a short time on a steam-bath. The product, isolated in the usual way, was in each case methyl Δ^{β}-dihydromuconate, m. p. 16°.

Ethyl ββ′-Diphenyl-ββ′-dihydroxyadipate.—The *meso*- and *racemic* forms of this ester were obtained in essentially the way described by Beschke (*loc. cit.*); magnesium, however, was employed instead of zinc, the reaction being started by addition of a crystal of iodine.

Action of Phosphorus Halides on Dihydroxy-esters.—Both *meso*- and *racemic* forms yielded, when allowed to stand for 24 hours with the calculated amount (2 mols.) of phosphorus tribromide, diphenylmuconic esters. Simple replacement of hydroxyl by bromine could not be effected, the bromine content of the product never rising to 1%. The *meso*-ester (m. p. 168°) yielded invariably and solely an *ethyl* ββ'-*diphenylmuconate* which crystallised from benzene or alcohol in short prisms, m. p. 136° (Found: C, 75·6; H, 6·3. $C_{22}H_{22}O_4$ requires C, 75·5; H, 6·3%). The *racemic* ester (m. p. 137°) similarly yielded a second, more soluble form of the same ester which crystallised from the same solvents in well-defined needles, m. p. 174° (Found: C, 75·6; H, 6·3%).

Treatment of benzene solutions of the hydroxy-esters with phosphorus pentabromide or pentachloride gave similar results. Moderation of the reaction by cooling to 0° did not prevent the removal of hydrogen bromide.

Isomerisation of Ethyl Diphenylmuconate, m. p. 174°.—The pure dry ester, when allowed to stand in the air for 15 minutes, became sticky. Recrystallisation at this stage yielded a mixture of ethyl diphenylmuconates, m. p.'s 174° and 72°. When the sticky mass was allowed to stand longer (45 minutes), it set to a glassy solid which crystallised from alcohol in small needles, m. p. 72° (Found: C, 75·55; H, 6·3%). Yield 95%. The rapid isomerisation of the form, m. p. 174°, prevented satisfactory observations of the geometrical form of its reduction product.

Preparation of Isomeric Ethyl ββ'-*Diphenylmuconates*.—For the preparation of considerable quantities of these esters the phosphorus halide method was inconvenient. The following methods were therefore employed.

(*a*) The dihydroxy-ester was refluxed with zinc dust (3 parts) and absolute alcohol (8—10 parts) for 6 hours. In the case of the *meso*-ester, crystallisation of ethyl diphenylmuconate (m. p. 136°) from the hot filtered solution commenced at once; with the *racemic* ester, concentration was necessary before the unstable form (m. p. 174°) separated. This process gave excellent results with the pure dihydroxy-esters.

(*b*) The dihydroxy-ester was boiled for 1 hour with acetic anhydride and the product was cooled and extracted with petroleum (b. p. 80—100°) (in which acetic anhydride is not very soluble). Evaporation of the solvent and cooling of the residue to 0° caused crystallisation of the dehydrated ester. This method was usually employed for treating the residual sludge of the "Reformatski" product. This contained a considerable quantity of difficultly recoverable *racemic* ester which yielded directly, on dehydration for 24 hours, a crystalline product purifiable by one recrystallisation.

ββ'-*Diphenylmuconic Acid*.—Hydrolysis of ethyl diphenylmuconate, m. p. 136°, with dilute sulphuric acid yielded the corresponding acid, which separated from alcohol as a white, crystalline powder, m. p. 142° [Found: C, 73·1; H, 4·7; *M* (dibasic), 298. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%; *M*, 294]. The isomeric ester, m. p. 72°, yielded, on similar treatment, an acid, m. p. 181°. This also separated from alcohol as a white, crystalline powder (Found: C, 73·6; H, 4·7%; equiv., 221) and was probably identical with Beschke's 2 : 3-diphenylcrotonolactone-3-acetic acid.

Reduction of Isomeric Ethyl Diphenylmuconates.—The two stable esters were separately hydrolysed by adding a hot aqueous solution of caustic soda to a boiling alcoholic solution of the ester until permanent alkalinity was secured. After the alcoholic liquor had been boiled for 1 hour, the precipitated sodium salt was filtered off and dissolved in a small quantity of water. Gradual addition of 3% sodium amalgam until effervescence ceased, followed by filtration and acidification, gave an immediate precipitate of the reduced acid. cis-ββ′-*Diphenyl*-Δ^{β}-*dihydromuconic acid*, the sole product from ethyl diphenylmuconate (m. p. 136°), crystallised from water in colourless prisms, m. p. 195° (Found: C, 72·9; H, 5·2. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·3%). trans-ββ′-*Diphenyl*-Δ^{β}-*dihydromuconic acid*, which was produced together with its isomeride from ethyl diphenylmuconate (m. p. 72°), crystallised from alcohol in colourless prisms, m. p. 297° (Found: C, 72·9; H, 5·3%). The *ethyl* esters of the *cis*- and *trans*-acids, obtained by saturating alcoholic solutions with hydrogen chloride, crystallised from alcohol in colourless prisms, m. p. 56° and 86°, respectively.

Oxidation of Δ^{β}-*Diphenyldihydromuconic Acids.*—Each of the acids (3 g.) was separately dissolved in a slight excess of dilute sodium carbonate solution and treated with a rapid current of ozonised oxygen for 48 hours. After air had been bubbled through the brown liquids to remove dissolved ozone, the products were acidified and extracted with ether. The ethereal extract contained in each case a mixture of unchanged acid and benzoylacetic acid, which were separated by fractional crystallisation from benzene and petroleum. The benzoylacetic acid derived from each acid, after the final crystallisation from alcohol, melted and decomposed at 103—104° and gave a violet-red coloration with ferric chloride (Found: C, 65·7; H, 4·9. Calc.: C, 65·8; H, 4·9%).

The authors desire to acknowledge grants from the Government Grant Committee of the Royal Society (to E. H. F.) and the Chemical Society (to W. M. D.) towards the expenses of this research.

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[*Received, December 2nd*, 1926.]

LXI.—*The Reaction between Grignard Reagents and 10-Chlorophenoxarsine or 10-Chloro-5 : 10-dihydrophenarsazine.*

By John Alfred Aeschlimann.

The method of preparing 10-ethylphenoxarsine by heating 10-chlorophenoxarsine with magnesium ethyl bromide described by the author (J., 1925, **127**, 813) has been extended to the 10-*methyl* and 10-*phenyl* compounds, derivatives of which have been prepared. 10-Methylphenoxarsine can be readily obtained by performing the Grignard reaction in the cold as described by Roberts and Turner (J., 1926, 1210), who, although they did not isolate any arsine, claimed that their method is of general application. That this is not the case follows from the experimental results described below, and agrees with the previous work of Lewis, Lowry, and Bergheim (*J. Amer. Chem. Soc.*, 1921, **43**, 890), who failed to isolate either the phenyl- or the ethyl-phenoxarsine under similar conditions, but mistook for the latter a compound, m. p. 218°, which was probably phenoxarsinic acid, m. p. 219°, as this can be isolated by allowing the oxide formed in the reaction to oxidise in air. Of the above three arsines, only the phenyl derivative is crystalline.

In several attempts to obtain 10-phenylphenoxarsine by the condensation of diphenyl ether with phenyldichloroarsine in presence of aluminium chloride, only 10-chlorophenoxarsine was obtained. This result is analogous to that obtained by Burton and Gibson (J., 1926, 465) in the condensation of diphenylamine and phenyldichloroarsine, although they used no catalyst to facilitate the decomposition of the dichloroarsine to arsenious chloride. 10-Chlorophenoxarsine does not give 10-phenylphenoxarsine on being heated with benzene and aluminium chloride.

10-Chloro-5 : 10-dihydrophenarsazine reacts with two molecules of the respective Grignard reagents to give 10-*methyl*-5 : 10-*dihydrophenarsazine*, 10-*ethyl*-5 : 10-*dihydrophenarsazine*, and 10-*phenyl*-5 : 10-*dihydrophenarsazine*, hydrocarbons also being formed owing to the presence of the NH-group. When the reaction mixture is cooled during addition of the chloroarsine, the formation of hydrocarbon does not take place and the heavy oil which separates from the ethereal solution should contain the : NH(MgI)R group. Treatment of this with methyl iodide, however, does not produce 5 : 10-dimethyl-5 : 10-dihydrophenarsazine, but 10 : 10-*dimethyl*-5 : 10-*dihydrophenoxarsonium iodide*, which is also the product when the methylation of 10-methyl-5 : 10-dihydrophenarsazine is attempted under various conditions. The latter compound, unlike 10-chloro-5 : 10-dihydrophenarsazine (Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1), which loses hydrogen chloride from the 5 : 10-positions to produce phenarsazine when heated in a vacuum, loses methyl iodide under these conditions and re-forms 10-methyl-5 : 10-dihydrophenarsazine. The methyldihydrophenarsazine combines with ethyl iodide, and the ethyldihydrophenarsazine with methyl iodide, to form the same 10-*methyl* : 10-*ethyl*-5 : 10-*dihydrophenarsazonium iodide*. The formation of the arsonium rather than the ammonium compound by addition of alkyl iodide recalls the ease of formation of sulphonium compounds from the similarly constituted di-*p*-nitrodiphenylamine sulphoxide (Smiles and Hilditch, J., 1908, **93**, 145, 1687).

The observation of Turner, Sheppard, and Bolton (J., 1925, **127**, 547), that diphenylene disulphide is formed when a mixture of arsenic trichloride and diphenyl sulphide is heated with aluminium chloride, has been extended to the reaction between arsenic trichloride or phenyldichloroarsine and the double compound $(C_6H_5)_2S,AlCl_3$ (Böeseken, *Rec. trav. chim.*, 1905, **24**, 219). Equimolecular quantities of triphenylarsine, sulphur monochloride, and aluminium chloride similarly fail to produce a cyclic arsine, the product after treatment with water being triphenylarsine dihydroxide.

EXPERIMENTAL.

10-Methyl- and 10-ethyl-phenoxarsines were each prepared by the addition of 10-chlorophenoxarsine (10 g.) to the stirred Grignard reagent (2 mols.). The yields obtained after decomposition of the products as described by Roberts and Turner (*loc. cit.*) were : from MgMeI, 85% ; from MgEtI, 40% (impure); from MgEtBr, 20% (impure). 10-Phenylphenoxarsine was not isolated in this way, as it was difficult to separate from unchanged chlorophenoxarsine.

10-Ethylphenoxarsine was obtained in 80% yield by heating 10 g. of 10-chlorophenoxarsine in 60 c.c. of benzene with 1½ mols. of magnesium ethyl bromide in 50 c.c. of ether for 2½ hours. When only 1¼ mols. of the Grignard reagent were used as previously described, the yield was about 70%.

10-*Methylphenoxarsine* is a colourless oil, b. p. 185°/20 mm., 198—200°/40 mm. (Found : C, 60·7 ; H, 4·2. $C_{13}H_{11}OAs$ requires C, 60·5 ; H, 4·3%).

10-*Methylphenoxarsine dihydroxide*, m. p. 94°, was obtained by dissolving the arsine in excess of hydrogen peroxide solution, evaporating the water and recrystallising the residue from benzene (Found : C, 53·7 ; H, 4·45. $C_{13}H_{13}O_3As$ requires C, 53·4 ; H, 4·45%).

It is dehydrated to the oxide when heated in a vacuum at 50° (Found: loss, 5·9. Calc. for 1 H_2O; loss, 6·1%). The hydroxide is re-formed after 12 hours' exposure of the oxide to air.

10 : 10-Dimethylphenoxarsonium iodide forms white needles which melt at 225° when slowly heated and at 220° when rapidly heated in closed or in open tubes [Found: I (Carius), 31·7. Calc.: I, 31·7%]. Roberts and Turner (*loc. cit.*) give m. p. 207°.

10-Methyl-10-ethylphenoxarsonium iodide (Aeschlimann, *loc. cit.*) is less readily formed from 10-methyl- than from 10-ethylphenoxarsine and the requisite alkyl iodide. Only the white compound was isolated in the former case.

10-*Methyl*-10-*carboxymethylphenoxarsonium bromide*, m. p. 199°, was formed on heating equimolecular quantities of 10-methylphenoxarsine and bromoacetic acid for 15 minutes at 90°, the stirred mixture gradually becoming solid. The product was washed with ether and recrystallised from alcohol, in which it was not easily soluble (Found: Br, 20·3, 20·6; equiv. by titration with alkali, 394. $C_{15}H_{14}O_3BrAs$ requires Br, 20·2%; equiv., 397).

10-*Ethylphenoxarsine sulphide* was slowly formed by the action of hydrogen sulphide on an aqueous solution of the oxide, or by addition of excess of sulphur to a solution of 10-ethylphenoxarsine in carbon disulphide. It is soluble in ether, and crystallises from alcohol in long needles, m. p. 109° (Found: S, 10·1. $C_{14}H_{13}OSAs$ requires S, 10·6%).

10-*Phenylphenoxarsine* was obtained in 75% yield by heating the Grignard reagent prepared from 15 g. of bromobenzene with 10 g. of 10-chlorophenoxarsine in benzene for 4 hours. (The reaction is incomplete after 2½ hours' heating, and the unchanged chloroarsine is difficult to remove from the product, which boils at 270°/30 mm. and solidifies slowly.) It crystallised from alcohol in colourless needles, m. p. 107° (Found: C, 66·8; H, 4·1. $C_{18}H_{13}OAs$ requires C, 67·5; H, 4·1%).

10-*Phenyl*-10-*methylphenoxarsonium iodide*, m. p. 175°, did not appear to be formed until the reactants were heated (Found: I, 27·6. $C_{19}H_{16}OIAs$ requires I, 27·5%).

10-*Phenylphenoxarsine oxide*, m. p. 184°, was formed by dehydrating the hydroxide in a vacuum at 50° (Found: C, 64·2; H, 3·8. $C_{18}H_{13}O_2As$ requires C, 64·4; H, 3·9%). The hydroxide was obtained by the action of hydrogen peroxide, or of sulphur monochloride and water (Zuckerkandl and Sinai, *Ber.*, 1921, **54**, 2484), on 10-phenylphenoxarsine. It is deliquescent, and retains 1½ mols. of water on drying to constant weight in a desiccator; it then melts at 93° (Found: loss on conversion into oxide, 7·2. Calc. for 1½H_2O: loss, 7·4%).

10-*Methyl*-5 : 10-*dihydrophenarsazine* was obtained by the addition of 14 g. of powdered 10-chloro-5 : 10-dihydrophenarsazine in three portions to the Grignard reagent (2·1 mols.) prepared from 16 g. of methyl iodide and 2·6 g. of magnesium in 50 c.c. of ether. (Usually ebullition and evolution of hydrocarbon vapours were allowed to occur, and immediate solution then took place. If, however, the reagent was cooled in a freezing mixture during the addition, gas was not evolved and two layers were formed. When this mixture was heated with methyl iodide, only the arsonium iodide and the methyl arsine were formed.) The mixture was heated for a short time to complete the reaction and then decomposed in the usual manner; the residue crystallised after evaporation of the ether from the extract. After recrystallisation from hot alcohol, the *dihydrophenarsazine* melted at 105°, and was soluble in the usual solvents except light petroleum. It was usually yellow, but formed almost colourless plates after being recrystallised several times (Found: C, 60·6; H, 4·0. $C_{13}H_{12}NAs$ requires C, 60·7; H, 4·1%).

10-*Ethyl*-5 : 10-*dihydrophenarsazine*, obtained in a similar way, melted at 75° (Found: C, 62·0; H, 5·0. $C_{14}H_{14}NAs$ requires C, 62·0; H, 5·2%).

10-*Phenyl*-5 : 10-*dihydrophenarsazine*, m. p. 142°, was less soluble in alcohol than the alkyldihydrophenarsazines, and required heating for its formation (Found: C, 68·1; H, 4·4. $C_{18}H_{14}NAs$ requires C, 67·7; H, 4·4%).

All three arsines reacted with methyl iodide to form arsonium iodides, crystallisable from hot alcohol and only slightly soluble in water. The methyl compound reacted in the cold, the others required heating. Even in presence of a large excess of methyl iodide in a sealed tube at 100°, only one molecule of the iodide took part in the reaction; a similar combination took place at the ordinary temperature.

10 : 10-*Dimethyl*-5 : 10-*dihydrophenarsazonium iodide* has m. p. 259° (slow heating), 268° (rapid heating) (Found: C, 42·1; H, 3·6; I, 31·7. $C_{14}H_{15}NIAs$ requires C, 42·2; H, 3·8; I, 32·0%).

10-*Methyl*-10-*ethyl*-5 : 10-*dihydrophenarsazonium iodide*, m. p. 236° (rapid heating), 229° (slow heating), was obtained from either the methyl or the ethyl compound and the appropriate alkyl iodide (Found: I, 30·4. $C_{15}H_{17}NIAs$ requires I, 30·7%).

10-*Phenyl*-10-*methyl*-5 : 10 *dihydrophenarsazonium iodide* has m. p. 158° (decomp.) (Found: I, 27·9. $C_{19}H_{17}NIAs$ requires I, 27·6%).

5-*Acetyl*-10-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 154°, was obtained by boiling the arsazine with an excess of acetic anhydride for 1 hour, removing the latter in a vacuum, and crystallising the product from alcohol. It is less soluble in ether than the arsazine (Found : C, 60·6; H, 4·5. $C_{15}H_{14}ONAs$ requires C, 60·2; H, 4·7%).

In conclusion, I express my thanks to the authorities of the Chemical Departments at Battersea Polytechnic and Cambridge University for providing the necessary facilities for this research.

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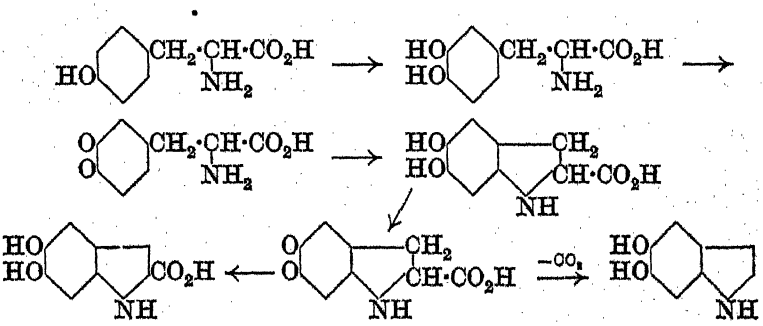
[*Received, December 3rd,* 1926.]

LXII.—*Synthesis of 5 : 6-Dimethoxyindole and its 2-Carboxylic Acid.*

By ALBERT EDWARD OXFORD and HENRY STANLEY RAPER.

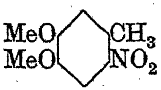
IT has been recently shown by Raper (*Biochem. J.*, in the press) that when tyrosine is oxidised by the enzyme tyrosinase, a series of changes occurs which results in the production of 5 : 6-dihydroxyindole and to a lesser extent of 5 : 6-dihydroxyindole-2-carboxylic acid. These changes, which represent a new type of indole synthesis, are as follows :



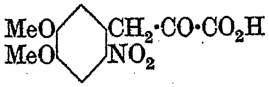
Both 5 : 6-dihydroxyindole and its 2-carboxylic acid are very easily oxidised and can only be isolated as dimethoxy-compounds by methylation in a neutral atmosphere. For purposes of identification, it was necessary to synthesise them, since they had not been previously prepared. Perkin and Rubenstein (J., 1926, 357) have described a synthesis of ethyl 5 : 6-dimethoxyindole-2-carboxylate, but the yields were poor and the ester was not easily converted into the free acid because the latter tended to produce tarry products on heating in the presence of acids.

Attempts to obtain 5 : 6-dimethoxyindole by condensing *as*-dichlorodiethyl ether with 4-aminoveratrole (compare Berlinerblau, *Monatsh.*, 1887, 8, 180) proved fruitless. The method finally adopted was that used by Blaikie and Perkin (J., 1924, **125**, 296) in the preparation of certain of the monomethoxyindoles.

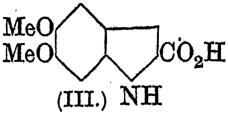
6-Nitrohomoveratrole (I), when condensed with ethyl oxalate in the presence of potassium ethoxide, yields 2-nitro-4 : 5-dimethoxyphenylpyruvic acid (II), from which 5 : 6-dimethoxyindole-2-carboxylic acid (III) is obtained by reduction with ferrous sulphate and ammonia.



(I.)



(II.)



(III.)

The last-named acid loses carbon dioxide at its melting point, yielding 5 : 6-dimethoxyindole.

The series of changes described above which tyrosine undergoes as a result of the action of the enzyme tyrosinase is completed by the formation of a black, insoluble pigment—melanin. This is produced undoubtedly by the oxidation in air of 5 : 6-dihydroxyindole. Similar pigments are produced in nature, both in animals and in plants, and they are known to contain within their molecule some cyclic structure in which nitrogen is present. The production of dihydroxyindole from tyrosine indicates, therefore, that the nitrogen-containing cyclic structure is present before melanin is formed and suggests that tyrosine and not tryptophan may be the chief mother-substance of melanin pigments in nature.

The first stage of the oxidation brought about by the enzyme, *i.e.*, the production of 3 : 4-dihydroxyphenylalanine from tyrosine, is of considerable interest in that it shows a possible method by which certain pyrocatechol derivatives may arise in nature. The 3 : 4-dihydroxy-grouping—often methylated—is of relatively frequent occurrence, *e.g.*, in adrenaline, 3 : 4-dihydroxyphenylalanine, vanillin, eugenol and other naturally occurring products.

EXPERIMENTAL.

2-*Nitro*-4 : 5-*dimethoxyphenylpyruvic Acid* (II).—Potassium (9·9 g.) was pulverised under boiling benzene (250 c.c.). After the liquid had been allowed to cool, and ether (250 c.c., dry and free from alcohol) had been added, a solution of 100% alcohol (14·5 c.c.) in dry ether (15 c.c.) was slowly run in with shaking, after which the mixture was kept for ½ hour. Ethyl oxalate (37·2 g.) was now added followed by a solution of 6-nitrohomoveratrole (50 g.) in dry benzene (300 c.c.). The mixture, protected from atmospheric moisture and carbon dioxide, was kept at 35—40° for 24 hours with occasional shaking.* Water (500 c.c.) was now added to dissolve the cake of the potassium derivative of 2-nitro-4 : 5-dimethoxyphenylpyruvic acid which had separated, and the purple aqueous layer, after separation, was washed with a little benzene and acidified with a slight excess of dilute hydrochloric acid. A copious sandy precipitate of the above acid was immediately formed, which when dried was sufficiently pure for use in the next stage of the synthesis. A further small amount could be isolated by exhaustively extracting the combined benzene–ether layers with 5% caustic soda solution and then acidifying the alkaline extract. The total yield was 40 g. or 60% of the theoretical, and most (16 g.) of the unchanged 6-nitrohomoveratrole was recovered by evaporation of the combined benzene–ether layers.

2-Nitro-4 : 5-dimethoxyphenylpyruvic acid is sparingly soluble in water and readily soluble in the usual organic solvents with the exception of light petroleum, and glacial acetic acid, from which it crystallises in clusters of bright yellow, microscopic needles, m. p. 193—194°, with evolution of gas at 197° (Found : C, 48·85; H, 4·0. $C_{11}H_{11}O_7N$ requires C, 49·1; H, 4·1%). It dissolves in dilute aqueous caustic soda to a deep permanganate-purple solution, the colour being discharged on long standing. Its aqueous-alcoholic solution gives a deep greenish-black colour with ferric chloride stable to acetic acid but destroyed by dilute mineral acids.

The *phenylhydrazone* was obtained by boiling a solution of the acid (0·32 g.) and phenylhydrazine (0·13 g.) in glacial acetic acid (20 c.c.) for 30 minutes. On dilution with much water the phenylhydrazone separated as a sandy precipitate which was crystallised first from benzene and then from 50% acetic acid, from which it separated in minute plates (parallelipipeds) which darken at 165° and melt at 170° with vigorous decomposition (Found: C, 57·3; H, 5·15. $C_{17}H_{17}O_6N_3$ requires C, 56·8; H, 4·8%).

2-*Nitro*-4 : 5-*dimethoxyphenylacetic Acid*.—The pyruvic acid (0·42 g.), dissolved in 2% caustic soda solution (3·5 c.c.) and cooled in ice, was oxidised by the careful addition of hydrogen peroxide (20 volume; 8 c.c. in all) until the colour had been discharged; more 2% caustic soda solution and hydrogen peroxide were then cautiously added until the liquid was permanently decolorised. The pale yellow precipitate obtained on acidification was collected and crystallised from dilute acetic acid, from which it separated in almost colourless needles, m. p. 202—204° with slight decomposition to a red liquid (Found: C, 50·2; H, 4·5. $C_{10}H_{11}O_6N$ requires C, 49·8; H, 4·6%). It is readily soluble in ethyl acetate and glacial acetic acid, and sparingly soluble in benzene, chloroform, and cold water.

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* The mode of effecting the condensation described by Kermack, Perkin, and Robinson (J., 1921, **119**, 1630) which gave good results with *o*-nitro-*p*-tolyl methyl ether, *viz.*, digestion of the *o*-nitrotoluene with an alcoholic solution of sodium ethoxide and ethyl oxalate, is not to be recommended for the above, since one obtains a gummy product, very difficult to purify and not giving satisfactory results if used as such for the preparation of the indolecarboxylic acid.

5 : 6-*Dimethoxyindole-2-carboxylic Acid* (III).—2-Nitro-4 : 5-dimethoxyphenylpyruvic acid (38 g. of crude product) was dissolved in ammonia (213 c.c., *d* 0·880, mixed with 300 c.c. of water) and reduced by the addition of a hot solution of ferrous sulphate (274 g. of hydrated crystals in 300 c.c. of water). The mixture was heated on the steam-bath for 30 minutes with frequent shaking, and finally gently boiled for the same length of time. The liquid was filtered while hot, and the precipitate of ferric oxide washed with hot water containing a little ammonia. The dark brown filtrate was acidified by the addition of a very slight excess of *N*-sulphuric or, preferably, *N*-phosphoric acid, and the precipitated indolecarboxylic acid at once filtered off and dried in a vacuum. The yield is poor, but can be increased somewhat by immediately extracting the mother-liquor with ether. Purification of the acid is best effected by crystallising it first from hot water (charcoal) and then repeatedly from benzene, from which it separates in colourless plates, m. p. 202—203° (decomp.). Well-formed, rhombohedral tablets are deposited if a hot solution of the acid (0·5 g.) in acetone (10 c.c.) and benzene (100 c.c.) is allowed to cool slowly. The acid can also be crystallised from chloroform, in which it is sparingly soluble in the cold (Found: C, 59·9; H, 5·3. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). On warming with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid a pale purple colour is obtained which becomes redder on the addition of a trace of nitrite.

When a trace of nitric acid is added to a very dilute solution of the acid in glacial acetic acid, a yellow colour is developed, deepening to golden-yellow on warming. The acid itself dissolves in concentrated sulphuric acid to an orange solution, but addition of a trace of nitric acid merely brings about partial decoloration to pale yellow.

Attempts to obtain the ethyl ester (already described by Perkin and Rubenstein, *loc. cit.*) by the ordinary methods were unsuccessful owing to the instability of the acid in presence of mineral acids.

5 : 6-*Dimethoxyindole.*—5 : 6-Dimethoxyindole-2-carboxylic acid, contained in a small Claisen flask with a long side-arm, was heated in an oil-bath at 205—215° for ½ hour. When a quiet melt had been obtained, the flask was transferred to a fusible-metal bath, and its

contents distilled in a vacuum. The indole came over at 198°/8 mm. and solidified at once in the side-arm, which was afterwards severed from the flask and ground up with dilute potassium carbonate solution, and the solid material collected and extracted with boiling 95% alcohol, from which the indole separated, on cooling, in a state of purity, m. p. 154—155° unaltered by further crystallisations. 5 : 6-Dimethoxyindole crystallises from benzene in rods, from 95% alcohol and from light petroleum (in which it is very sparingly soluble) in colourless, glistening leaflets, and from 50% alcohol, by slow deposition, in long, coarse needles (Found : C, 67·6; H, 6·2; N*, 8·2; MeO, 34·0. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2; N, 7·9; MeO, 35·0%).

This indole quickly darkens on keeping and is very sensitive to oxidising agents in the presence of acids. Although insoluble in cold, dilute hydrochloric acid, it slowly develops a brown colour in contact with this acid, and, on warming, dissolves with almost immediate production of the brown colour. Addition of ferric chloride to an aqueous-alcoholic solution of the indole produces a permanent deep green coloration. With *p*-dimethylaminobenzaldehyde and hydrochloric acid the indole gives a rich purple colour and on addition of a trace of nitrite this changes to a deep crimson.

When equivalent quantities of the indole and of picric acid were dissolved in hot acetone or methyl alcohol, a deep red solution was obtained; this, on evaporation, yielded a deep purple, gummy picrate, which could not be obtained crystalline.

1-*Acetyl*-5 : 6-*dimethoxyindole* is formed in poor yield when 5 : 6-dimethoxyindole (0·4 g.) is boiled for 5½ hours with acetic anhydride (10 c.c.) and freshly-fused sodium acetate (1·2 g.). The cooled mixture is diluted with ether and filtered, and the filtrate evaporated in a vacuum, finally at 80°. The red, oily residue is then repeatedly extracted with boiling light petroleum (b. p. 60—80°), from which the acetyl derivative crystallises in minute, yellowish-brown, ill-defined leaflets, m. p. 150—152° (Found : C, 66·4; H, 6·2. $C_{12}H_{13}O_3N$ requires C, 65·8; H, 6·0%). A mixture of the indole and this derivative melted at 144—147°.

Neither 5 : 6-dimethoxyindole nor its 1-acetyl derivative gives the brucine reaction (compare Perkin and Rubenstein, *loc. cit.*, on ethyl 5 : 6-dimethoxyindole-2-carboxylate). In each case addition of a little nitric acid to a very dilute solution of the substance in glacial acetic acid produces a yellow tint only, changing to golden-brown on gentle warming. On standing, the colour becomes brownish-red. The indole gives no coloration, and the acetyl derivative a pale green colour, with concentrated sulphuric acid, but in each case addition of a trace of nitric acid at once produces an intense greenish-brown colour, changing quickly to brownish-red and, on standing, to pure red.

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* All the compounds described in this communication were analysed for nitrogen by the Pregl–Dumas method, and high results (0·3—1·5%) were consistently obtained. It seems well established that certain anisyl and veratryl derivatives during combustion are liable to give off methane, which gas is not completely oxidised when passed over hot copper oxide (compare Bradley and Robinson, J., 1926, 2361).

THE UNIVERSITY, MANCHESTER. [*Received, December 22nd, 1926.*]

LXIII.—*The Soluble Alkaline-Earth Aluminates.*

By HUBERT THOMAS STANLEY BRITTON.

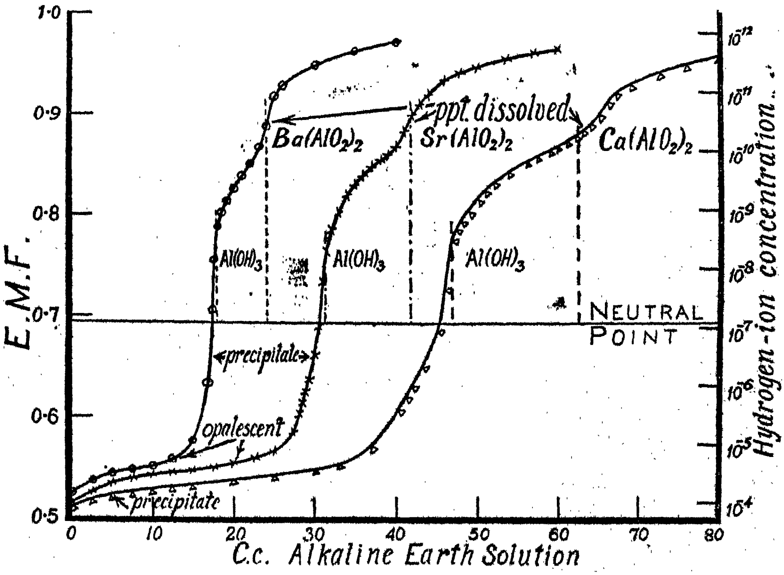
It is often stated that the aluminates of calcium, barium, and strontium are very sparingly soluble in water. Thus Marais (*Soil Science*, 1922, **13**, 368) asserts that lime removes alumina from a "soil solution" as a very sparingly soluble calcium aluminate, $Ca_3Al_2O_6$. Alumina, besides being present in soil solutions of which the hydrogen-ion concentrations are greater than that at which aluminium hydroxide begins to be precipitated, *viz.*, $10^{-4\cdot2}$ (compare Britton, J., 1925, **127**, 2121), is sometimes found in slightly alkaline soil solutions, of p_H about 9 (Magistad, *Soil Sci.*, 1925, **20**, 181). Pollard and Keast (private communication) found that it passed into the soil solution at p_H 7·7—8·6, as the result of treating soil with slaked lime, and, moreover, they observed that the aluminium content increased with the calcium content. It was suspected that the explanation lay in the formation of a soluble calcium aluminate. In order to test this supposition, the following titrations of dilute solutions of aluminium salts were carried out with solutions of each of the alkaline earths, the concentrations of which are given in Table I, and the changes in hydrogen-ion concentration were determined by means of the hydrogen and normal calomel electrodes, in the manner described in previous papers (J., 1924, **125**, 1572; 1925, **127**, 2110), the junction being a saturated solution of potassium chloride. The temperature was 20°.

The curves (see Fig. 1.) are similar to that obtained by using sodium hydroxide (J., 1925, **127**, 2121). The p_H's at which precipitation began in the three reactions are widely different, although those sections of the three curves which correspond to the formation of aluminium hydroxide cover approximately the same variation in hydrogen-ion concentration. Thus in the lime titration, in which the sulphate was employed, precipitation began when only

TABLE I.

Reactant.	Solution : 100 c.c. of	Precipitation began at p_H.	Precipitation began at Equivs. alkali per atom Al.	Precipitate dissolved at p_H.	Precipitate dissolved at Equivs. alkali per atom Al.
0·0447N-$Ca(OH)_2$.	0·00349M-$Al_2(SO_4)_3$.	4·14	0·32	10·17	3·90
0·0558N-$Ba(OH)_2$.	0·00333M-$AlCl_3$.	Opalescent. 4·76	2·09		
		Coagulated. 6·50	2·71	10·43	4·02
0·0391N-$Sr(OH)_2$.	0·00408M-$AlCl_3$.	Opalescent. 4·69	1·92		
		Coagulated. 6·50	2·88	10·60	4·02

FIG. 1.



0·32 equiv. of alkali per atom of aluminium had been added, whereas in both the strontia and baryta titrations, in which aluminium chloride was used, the solutions remained clear until 2·09 equivs., p_H 4·76, and 1·92 equivs., p_H 4·69, respectively, of alkali had been added; only opalescence was then produced, coagulation of the precipitates not occurring until 2·71 and 2·88 equivs., respectively, had been added, and a considerably higher p_H attained, *viz.*, 6·5. This delay in precipitation, despite the fact that the requisite precipitation p_H, 4·14, had been exceeded, and that nearly the total stoicheiometrical quantity of alkali had been added, is due to the characteristic tendency of chlorides to promote the formation of colloidal solutions—the dispersed particles formed in the initial stage of the reactions being too small to affect the appearance of the solution to the unaided eye. A similar instance is that of the chloride and sulphate of zirconium (Britton, J., 1925, **127**, 2125).

The solutions became neutral when the alkaline earths had been added in amounts slightly less than those required for the formation of aluminium hydroxide owing to the retention by the precipitates of some of the acid radical present in the original salts. In each of the titrations, the precipitates redissolved completely when approximately another equivalent of alkaline earth had been added, the dissolutions being reflected in the characteristic aluminate inflexions of the titration curves extending over a p_H range from 8 to 10·5. Magistad's results (*loc. cit.*) on the solubility of alumina in sodium hydroxide solutions of varying p_H are important in that they show that the solubility first becomes perceptible at p_H 7·55, being then 2 parts per million; at p_H 8·35, the solubility is 8·4 parts, but thereafter it increases rapidly to 34·6 parts per million at p_H 8·95. In a natural soil solution it was 31·0 parts per million at p_H 9·01. Hence it appears probable that the formula $M^{\cdot\cdot}(AlO_2)_2$ represents the type of combination in which the alkaline earths and alumina exist in solution.

It should be mentioned that in the calcium titration a fine precipitate containing both calcium and aluminium began to separate at p_H 11·7 when 90 c.c. of lime water had been added. It follows, therefore, that the disappearance of alumina from "soil solutions" cannot be attributed, as Marais states, to the formation of an insoluble calcium aluminate, for the hydrogen-ion concentration of ordinary "soil solutions" never becomes so low as p_H 11·7. No precipitates were formed in the other two titrations, even although large excesses of the reactants were added. The conditions under which the solid aluminates of barium may exist have recently been investigated by Malquori (*Gazzetta*, 1926, **56**, 54).

The author acknowledges his indebtedness to the Department of Scientific and Industrial Research for a personal grant, and to Professor J. C. Philip, F.R.S., for kindly placing facilities at his disposal.

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[*Received, December 3rd*, 1926.]

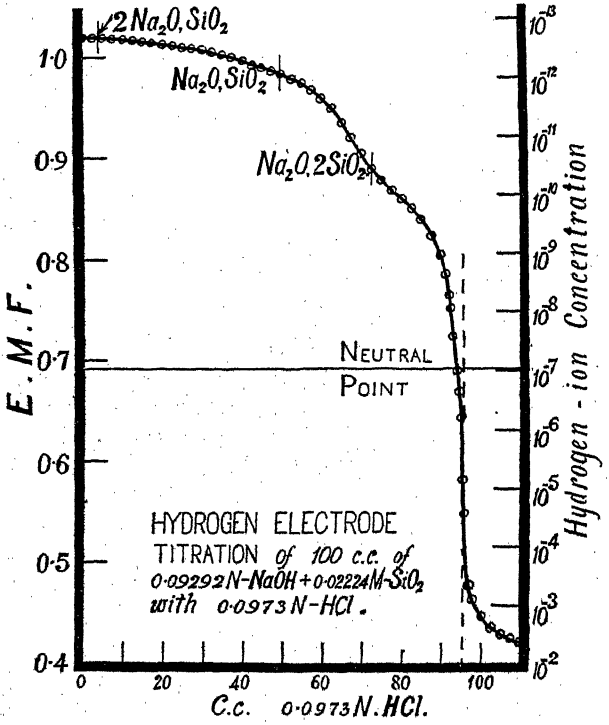
LXIV.—*Electrometric Study of the Precipitation of Silicates.*

By HUBERT THOMAS STANLEY BRITTON.

THE work now described was undertaken in order to gain some insight into the reactivity of silicic acid towards various bases of different strengths. Its reaction with sodium hydroxide was first studied, for, although this subject has received some attention in recent years by measurements of the hydrogen-ion concentrations of solutions of silicic acid in sodium hydroxide (Bogue, *J. Amer. Chem. Soc.*, 1920, **42**, 2575; Joseph and Oakley, J., 1925, **127**, 2814; Harman, *J. Physical Chem.*, 1926, **30**, 1100; Hägg, *Z. anorg. Chem.*, 1926, **155**, 20), there still remains much uncertainty as to the actual manner in which the acid ionises, and, moreover, the results hitherto recorded do not give a complete account of the variation in hydrogen-ion concentration throughout the course of neutralisation at 18°. Joseph and Oakley concluded, from p_H measurements at 33—38° of solutions of water-glass to which varying amounts of acid or alkali had been added, that the neutralisation curve obtained was "typical of the combination of a strong base with a weak dibasic acid," K_1 being about 10^{-10}, and K_2 about 10^{-12}, the symbols relating to the first and second dissociation constants, respectively. Hägg also states that, if silicic acid is not colloidal, K_1 of metasilicic acid is of the order of 10^{-9} and K_2 about 10^{-13}. The curve given in Fig. 1 shows the change in hydrogen-ion concentration when 100 c.c. of a solution, 0·09292N with respect to NaOH and 0·02224M with respect to SiO_2, were titrated at 18° with 0·0973N-hydrochloric acid, using the hydrogen and the normal calomel electrodes in the way previously described (J., 1924, **125**, 1572; 1925, **127**, 2110). The ratios of Na_2O to SiO_2 present in the solution at the different stages of neutralisation are indicated on the curve. Two inflexions occurred in that portion corresponding to the addition of 2 equivs. of sodium hydroxide to 1 mol. of silicic acid, and the point corresponding to half-neutralisation of metasilicic acid, *i.e.*, $Na_2O,2SiO_2$, falls at p_H 10·4 just at the beginning of the second inflexion. As other workers have shown, the ionisation of silicic acid cannot be represented satisfactorily in terms of two dissociation constants; moreover, the titration curve is not typical of a dibasic acid inasmuch as when K_1 and K_2 are widely different the point corresponding to half-neutralisation should lie somewhere about the middle of the second inflexion—in Fig. 1 it should be near the point corresponding to p_H 11. The curve, however, shows that silicic acid enters into some kind of combination with sodium hydroxide, and gives some idea of the hydrogen-ion concentrations that are thereby set up. It also shows that the hydrogen-ion concentration imparted by silicic acid to a solution is much too small to have any effect on the methyl-orange end-point, and hence the reason why the alkali present in a silicate solution may be titrated by using such an indicator.

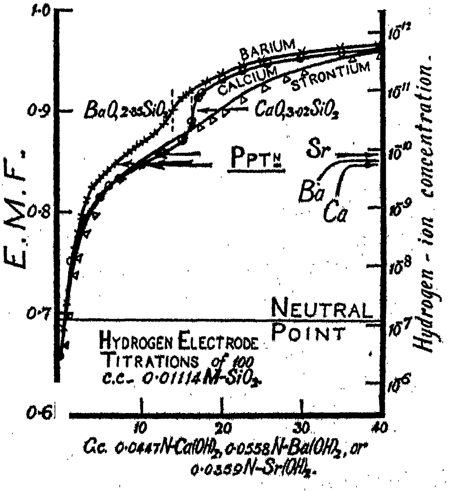
In order to study the reactions (and consequent precipitations) between silicic acid and the alkaline earths, hydrogen-electrode titrations were carried out at 18° of solutions of 100 c.c. of 0·01112*M*-SiO_2 with each of the following solutions: 0·0447*N*-calcium hydroxide, 0·0558*N*-barium hydroxide, and 0·0359*N*-strontium hydroxide. The solutions were prepared immediately before the titrations by neutralising sodium silicate solutions with hydrochloric acid, using methyl-orange, in order that they should contain the acid in a condition of maximum reactivity and that any diminution by ageing or by precipitation of the silicic acid should be avoided. These very dilute solutions were quite clear. The titration curves

FIG. 1.



given in Fig. 2 show that precipitation of the silicates did not begin until appreciable amounts of alkaline-earth solutions had been added, and when approximately the same hydrogen-ion concentrations had been attained. Thus the compositions of the solutes when on the point of precipitation were $CaO,5\cdot0SiO_2$; $BaO,5\cdot07SiO_2$; and $SrO,5\cdot54SiO_2$; the respective p_H's being 9·74, 9·72, and 9·90. In the case of the calcium and barium titrations marked inflexions occurred between p_H 10 and 11, but in the strontium titration an inflexion is scarcely perceptible. It was found that, in the calcium and barium reactions, these inflexions denoted the points when the silica and the whole of the added alkaline earths had become precipitated; hence the precipitates must have been $CaO,3\cdot02SiO_2,xH_2O$ and $BaO,2\cdot85SiO_2,xH_2O$. The hydrogen-ion concentrations of the solutions thereafter indicate that some further reaction took place between the precipitates and the additional alkaline-earth solutions. The hydrogen-ion concentrations of the solutions prior to precipitation are comparable with those produced with sodium hydroxide (*vide* Fig. 1), showing that the condition in which the silicic acid is present in both the alkali and the alkaline-earth solutions is similar. It seems reasonable to suppose that the high proportion of silica retained in the solutions must be due to some colloidal micellar formation.

Fig. 2.



The amounts of silica found in " soil solutions " of any p_H are very small even when their calcium contents are comparatively high. This seems to be contrary to what might be expected from the foregoing observations. The absorption of carbon dioxide, however, is sufficient to decompose any calcium silicate solutions which may be formed.

The absorption of alkaline earths by silica gel suspended in water was marked by a slow and gradual diminution in hydrogen-ion concentration. The curves showed a " buffer action," the extent of which depended on the amount of silica employed, commencing from p_H 6·5, instead of the sharp change shown in Fig. 2, where the silica was not in great excess. The buffer action of the silica gel is comparable with that which takes place when slaked lime is added to a soil, the reaction being usually between p_H 6·5 and 9.

Attention was now directed to the action of solutions of sodium silicate on typical metallic-salt solutions. The precipitates thus obtained have received comparatively little attention, and the very few formulæ which have been assigned to them show that the ratio of silica to base is always higher than that required to form the metasilicate. Some investigators have, however, mentioned that their precipitates contained free silica. The difficulties inherent in the separation of a silicate precipitate, often containing free silica, from its mother-liquor in anything approximating to the pure state (of which there is usually no criterion), are so great that it is probable that the few analyses which have been made convey no idea of the reaction which took place. It has been shown above that the acidic property of silicic acid asserts itself only in alkaline solutions, and consequently it would be expected that very little action could take place between it and those hydroxides which are precipitated from acid solutions, unless the substances formed by the interaction were extremely insoluble. The view has been advanced, however, to account for the acidity of "soil solutions," that complex aluminosilicic acids exist in the soil through the interaction of aluminium hydroxide and silica. If any such combination could take place, it is probable that it would have some effect on the hydrogen-ion concentration of the mother-liquor. It was therefore decided to investigate electrometrically the changes in hydrogen-ion concentration when solutions of sodium silicate and of metallic salts are allowed to interact. The sodium silicate employed was prepared from water-glass containing 2·16 mols. SiO_2 to 1 mol. Na_2O, and was 0·1020*N* with respect to sodium hydroxide. The impurities therein, including carbon dioxide, were so small as to have no measurable effect on the *E.M.F.* measurements. The solutions used are given in Table I, together with the p_H at which precipitation began, the amount of reactant which had to be added, and the p_H at which the respective hydroxides are precipitated, these values having been taken from the author's papers (J., 1925, **127**, 2110, 2120). 100 C.c. of salt solution were used for each titration.

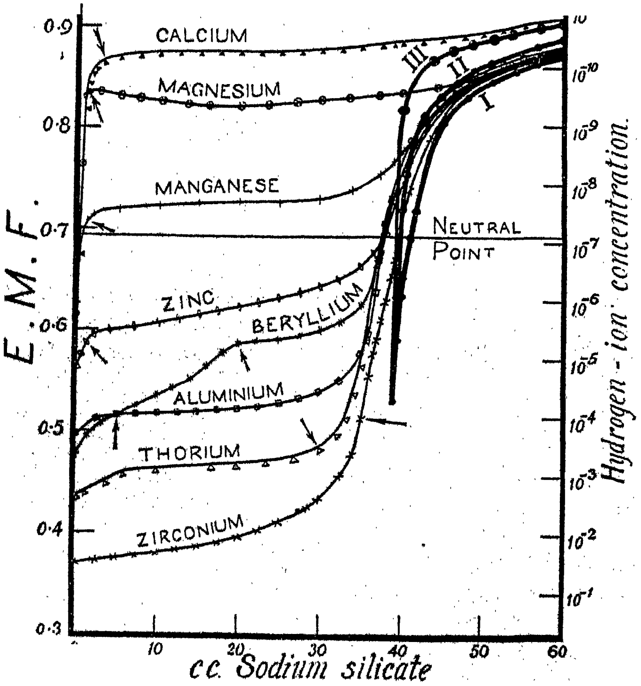
The titration curves are plotted in Fig. 3, in which the beginning of precipitation is marked by arrows. The amount of sodium silicate required in each reaction such that the alkali was in a quantity equivalent to the acid radical in 100 c.c. of salt solution was 39 c.c. The curves lying beyond 39 c.c. illustrate the effect of increasing amounts of sodium silicate on the hydrogen-ion concentration of the mother-liquor. The equation

$$Na_2O,2{\cdot}16SiO_2 + RCl_2 \longrightarrow 2NaCl + RO,xSiO_2\downarrow + (2{\cdot}16 - x)SiO_2$$

TABLE I.

Solution titrated.	Precipitation began at p_H.	Precipitation began at c.c. of sodium silicate.	Hydroxide precipitation at p_H.
0·01*M*-$ZrCl_4$.	3·98	35·0	1·86
0·01*M*-$ThCl_4$.	3·50	30·0	3·50
0·0067*M*-$Al_2(SO_4)_3$.	4·04	5·0	4·14
0·02*M*-$BeSO_4$.	5·31	20·0	5·69
0·02*M*-$ZnSO_4$.	5·25	1·0	5·20
0·02*M*-$MnCl_2$.	7·35	1·0	8·41
0·02*M*-$MgSO_4$.	9·50	1·0	10·49
[illegible]	10·07	3·0	—

FIG. 3.



shows that after the silicate $RO,xSiO_2$ had been precipitated by the 39 c.c., the mother-liquor comprised a sodium salt (chloride or sulphate), which through its very small concentration would have no measurable effect on the *P.D.*, and a certain amount of silicic acid which had escaped precipitation and would exert a buffering effect on the excess of sodium silicate. Some measure of the amounts of the silica which had remained in solution, and therefore of the amounts which had been precipitated with the metallic hydroxides, was obtained by following the changes in hydrogen-ion concentration when sodium silicate, of the same concentration as that used for the precipitations, was added to solutions having the volume attained when the precipitations had become complete, *viz.*, 139 c.c., and containing the same concentration of neutral sodium salt as the original mother-liquors but different amounts of silica. Thus Curve I (Fig. 3) represents the course taken when sodium silicate was added to 139 c.c. of solution containing 39 c.c. of sodium silicate exactly neutralised (to methyl-orange) with hydrochloric acid; it would therefore have been the curve obtained if the hydroxides alone had been precipitated and all the silica had remained in solution. Curve II shows the variation in hydrogen-ion concentration which would have been produced if the metasilicates of the metals had been precipitated, and the remainder of the silica had been left in solution; whereas Curve III corresponds to the change which would have occurred if all the silica present in the 39 c.c. had been precipitated. Except for the calcium curve, those sections of the curves corresponding to an excess of sodium silicate lie between Curves I and II. Hence the amounts of silica carried down with the various precipitates were somewhat smaller than that necessary for the formation of normal metasilicates. Table I shows that the p_H's at which the silicate precipitates of thorium, aluminium, and zinc separated were also those at which the respective hydroxides begin to be precipitated. In the case of the zirconium titration, the silicate precipitate did not appear until p_H 3·98 was reached, as compared with p_H 1·86 for the hydroxide when precipitated from chloride solution. The curve in the acid zone shows that the change in hydrogen-ion concentration was similar to that which occurred in the precipitations of the hydroxide, basic borate, and basic carbonate (J., 1926, 125). Precipitation was delayed until 3·59 equivs. of alkali had been added, whereas in the hydroxide precipitation opalescence appeared with 1·5 equivs. (Britton, J., 1925, **127**, 2133). Delayed precipitation was also noted with the basic borate and carbonate—3·4 equivs. of reactant being required in each case, and the p_H's being 4·07 and 3·95, respectively. It is remarkable that the silica in the reagent should have impeded the precipitation until an almost identical p_H, 3·98, had been attained. The other precipitate formed whilst the mother-liquor was still acidic was that of beryllium; this began to form at p_H 5·31, which is slightly lower than the hydroxide p_H, 5·69. As in previous work with beryllium, the precipitate did not begin to form until 1·01 equivs. of alkali, as sodium silicate, had been added. The difference in the two p_H's may be due the fact that the silicic acid sol formed in the course of the reaction became very unstable on approaching the neutral point. The p_H's at which the magnesium and manganese precipitates began to form are considerably less than those of the respective hydroxides. The cause probably lies in the insolubility of silicic acid, which cannot therefore retain a base in solution until the hydroxide p_H is reached. This is not the case with those precipitates which are formed in acid solutions, for then the acid liberated by the hydrolysis of the salts is sufficient to maintain solution until the corresponding hydroxide p_H is attained, or nearly so. The interaction of sodium silicate and a solution of calcium chloride produced a curve which shows that when the stoicheiometrical amount of alkali, as silicate, had been added, the alkalinity of the mother-liquor was greater than that which would have been set up if all the silica in the sodium silicate had been removed from solution by the calcium precipitate and an excess of alkali had been added instead of sodium silicate. In the other reactions investigated, it is probable that, owing to the great weakness of silicic acid, very little or no combination took place between it and the various hydroxides, the silica in the precipitates having been the result of simultaneous precipitations. It is nevertheless surprising that all the silica attached to those portions of the reagents which were responsible for the precipitations was not itself completely precipitated with the hydroxides. It is, of course, possible that the excess of sodium silicate which was subsequently added peptised some of the silica which had originally been precipitated. The formation of silicate precipitates is probably the result of the mutual coagulation of oppositely charged colloids through the removal by neutralisation of the substances which tended to stabilise or to peptise them, as found by Thomas and Johnson (*J. Amer. Chem. Soc.*, 1923, **45**, 2532) in the case of the mutual coagulation of a ferric hydrosol, peptised by ferric chloride, and a silica sol, peptised by sodium silicate.

The precipitation of calcium silicate is, however, of quite a different nature in that calcium hydroxide is fairly soluble in water and is, moreover, sufficiently strong a base to react with silicic acid. The alkalinity of the solution was caused by the considerable hydrolysis of the calcium silicate, and the exceptionally high p_H of the solution after 39 c.c. of sodium silicate had been added was apparently due to the withdrawal by the precipitate of more silica from the reagent, the precipitate thus containing more than 2 mols. of SiO_2 to 1 mol. of CaO.

Discussion.

The foregoing observations have an important bearing on the vexed question of the cause of soil acidity. In contrast with the large amount of work done to discover the cause of acidity in soils, very little has been done to ascertain what are the hydrogen-ion concentration relationships involved when any two of the constituents of the soil react. Swanson (*J. Agric. Res.*, 1923, **26**, 83) has shown that the acidity arises chiefly from the mineral constituents of the soil, the part played by the organic matter being, in general, negligible. The modern view is that the varying acidity of soils is due to the presence of complex aluminosilicic acids in different stages of neutralisation (*Ann. Reports*, 1925, **22**, 203). This idea appears to have been based on some work of Bradfield (*Missouri Agr. Exp. Sta. Research Bull.*, 1923, No. 60), who concluded from a comparison of the properties of soil colloids, separated from clay, with those of a mixture of hydrated silica, alumina, and ferric oxide, that the colloidal material consisted either of a definite compound or of a mixture of compounds in which the oxides were chemically bound as aluminosilicates. He considered that the type of titration curve obtained with the hydrogen electrode when a solution of calcium hydroxide was titrated with a clay suspension was that of a weak acid, and he was therefore led to believe that the colloidal material in the soil was itself the acid (*J. Amer. Chem. Soc.*, 1923, **45**, 2669). Saint (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 134) has suggested that if a soil be represented as a partly neutralised acid, the amounts of different bases which any particular soil can absorb should be in equivalent proportions, and has advanced evidence to support the view in the case of the alkalis and the alkaline earths when considered separately, the difference between the two sets of figures being attributed to the formation of insoluble alkaline-earth salts. This, however, would be expected from a consideration of the very similar reactions which the alkaline earths and the alkalis enter into with hydrated silica (compare Figs. 1 and 2).

The reaction involving the formation of the aluminium silicate precipitate affords no evidence of the existence of a complex aluminosilicic acid (Fig. 3). It is true that if the changes in hydrogen-ion concentration are followed when such a precipitate is subjected to treatment with solutions of alkalis or alkaline earths, the precipitate exerts a pronounced buffer action, which *primâ facie* might be regarded as indicating that the precipitate was an acid. This buffer action is, however, the result of a superposition of several reactions, *viz.*, (*a*) the reaction between the aluminium hydroxide and the base to form a soluble aluminate, buffering between p_H 8 and 10 (*vide* Britton, this vol., p. 424), (*b*) the reaction between the base and the hydrated silica, giving rise to a gradual rise in p_H from 6 upwards, and (*c*) an equilibrium between the silicic acid and any soluble aluminate, *e.g.*, $Ca(AlO_2)_2$, which may have been initially formed, to give calcium silicate, $CaO,xSiO_2,yH_2O$, and hydrated alumina, producing a hydrogen-ion concentration from p_H 6 upwards.

The amount of soluble aluminate actually formed is doubtless a function of the amount of water present. Similarly, if the inorganic colloids of the soil be considered as mixtures chiefly of hydrated alumina and silica, then the effect on the hydrogen-ion concentration of adding slaked lime to the soil would be determined by the reactivity of the two constituents with the lime. The titration curves of Hissink and van der Spek (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 72) with the hydrogen electrode of soil suspensions all show buffer action between p_H 6 and 8.

The curves given in Fig. 3 also account for the presence of various metals in soil solutions of different p_H reactions. Magistad (*Soil Sci.*, 1925, **20**, 181) has found that aluminium appears in soil solutions only when the p_H is lower than 4·0—4·5 or higher than 8. The limit on the acid side is seen to correspond with the p_H range at which aluminium hydroxide or silicate is precipitated (Fig. 3), and, as pointed out previously (this vol., p. 424), its reappearance in alkaline solutions is due to the acidic behaviour of the aluminium hydroxide exerting itself. Many chemists have also found alumina in the neutral-salt extracts of sour soils; thus, by the use of potassium chloride or nitrate, sodium chloride, etc., Veitch (*J. Amer. Chem. Soc.*, 1904, **26**, 637) concluded that the addition of sodium chloride to a soil did not liberate hydrochloric acid as such but aluminium chloride, and therefore the acidity was only apparent. Knight's (*Ind. Eng. Chem.*, 1920, **12**, 343) analysis of a soil extract with potassium nitrate shows that 90% of the titratable acid was in combination with alumina. Rice (*J. Physical Chem.*, 1916, **20**, 214) found aluminium in potassium nitrate extracts of which the p_H's ranged from 3·5 to 4·5. Niklas and Hock (*Z. angew. Chem.*, 1925, **38**, 195) have titrated potassium chloride extracts of soils with sodium hydroxide, using the hydrogen electrode. The first branch of their curve, corresponding to the decomposition of the aluminium salt, lies at about p_H 4 (compare Fig. 3), and the remaining section shows a buffer action up to just above p_H 8. The acidity of the more acidic soils is due to the normal hydrolysis of the aluminium salts formed in the soil.

The p_H of soil solutions from sour soils after treatment with neutral salts often becomes still lower; thus Crowther (*J. Agric. Sci.*, 1925, **15**, 212) found that soils of p_H 4·78 on treatment with neutral salts gave about p_H 4. Soils of $p_H > 6$ appear to be unaffected by neutral salts, and their titratable or "mineral" acidity becomes negligible (compare Christensen and Jensen, *Trans. 2nd Comm. Internat. Soc. Soil. Sci.*, Gröningen, 1926, 111). The mineral acidity given by acid soils appears to depend on the extent to which neutral salts, when allowed to react upon soils, are able to cause an increase in hydrogen-ion concentration above that requisite for the precipitation of aluminium hydroxide, and thereby to enable alumina to pass into solution as a salt. The fact that the hydrogen-ion concentrations of such soil solutions are nearly the same as that at which aluminium hydroxide is normally precipitated suggests that the soil must contain some aluminium hydroxide in a partly neutralised state (*vide* Britton, J., 1925, **127**, 2120). This would, on hydrolysis through contact with water, give a p_H near that at which aluminium hydroxide becomes precipitable. When a neutral-salt solution is added to such a soil, it is probable that the salt splits up, the basic part combining with the preponderance of silicic acid and being retained by the soil, and the acidic part combining with the partly neutralised aluminium hydroxide to enable some aluminium salt to pass into solution. Thus sodium chloride might be considered to split up into sodium oxide and hydrochloric acid, the sodium oxide attaching itself to the large excess of colloidal silica and thus becoming insoluble, whereas the hydrochloric acid, in reacting with the aluminium hydroxide, causes some aluminium chloride to pass into solution and thereby increases the hydrogen-ion concentration and the titratable acidity. It is significant that this "exchange" acidity disappears almost completely from soils of p_H 6 and above. It is at this point that aluminium hydroxide acquires its optimum insolubility, due to the withdrawal of the small amount of acid radical which it retained on being precipitated. Above this point, it behaves as an acid and consequently is without effect on neutral salts.

Manganese has been found in solutions from certain acid soils. Pollard (private communication) has found it in solutions of p_H up to 6 from certain sour soils. Rice (*loc. cit.*) found it in potassium nitrate extracts up to p_H 5 of acid soils. Fig. 3 shows that the precipitation of manganese silicate does not begin until just above p_H 7. The p_H of manganous salt solutions is of the order 5—6, but it must be remembered that, when a manganous salt solution is treated with alkali in a quantity insufficient to start precipitation, the solution rapidly decomposes through oxidation and brown oxide separates. Hence it is unlikely that manganese would be found in a soil solution of $p_H > 6$.

Although ferric oxide is often a constituent of soils, very little can pass into the soil solution, except in colloidal form, because it is precipitated from strongly acid solutions (Britton, J., 1925, **127**, 2155). It can, however, sometimes be detected in the neutral-salt extracts of sour soils by testing with an alcoholic solution of potassium thiocyanate (Comber's test). Pollard (private communication) found that by adding hydrochloric acid to soils, the iron content of the aqueous extracts only became perceptible when the solutions had become more acid than p_H 1·5.

The phenomenon of base exchange as exemplified by soils has been attributed to the existence of zeolitic combinations in the inorganic colloidal matter, in spite of the fact that zeolites themselves do not occur in soils. The compositions of most of the zeolites may be expressed by the general formula

$$RO,Al_2O_3,xSiO_2,yH_2O,$$

where R may represent one atom of a bivalent metal or two of a univalent metal, and $x =$ or >2. For Gans's synthetic permutites x varied from 3 to 4. They were prepared by the action of alkali-metal aluminate solutions on silicic acid, and not by the action of alkali-metal silicate on aluminium hydroxide. It has been shown (Britton, *Analyst*, 1921, **46**, 363; J., 1925, **127**, 2120; this vol., p. 424) that the amounts of alkali or alkaline earth which dissolve aluminium hydroxide to form the soluble aluminate are approximately the same as those indicated by the formula R^IAlO_2, *viz.*, either 1 mol. R^I_2O or 1 mol. $R^{II}O$ to 1 mol. Al_2O_3. This happens to be the ratio found in zeolites. Calcium aluminate solution on reacting with silicic acid, as either sol or gel, decomposes between p_H 7 and 9 to give precipitates of calcium silicate (indefinite) and aluminium hydroxide, the aggregate composition of the precipitates being $CaO,Al_2O_3,xSiO_2,yH_2O$. Hence, it may be that the "base exchange" exhibited both by zeolites and by soils is due to the similarity of their active constituents.

Summary.

(1) The reactions between silicic acid and sodium hydroxide or the alkaline earths in solution, and those between solutions of typical metallic salts and sodium silicate, have been investigated by means of the hydrogen electrode.

(2) Although the mode of ionisation of silicic acid cannot be expressed in terms of dissociation constants, its reactions with the stronger bases have a pronounced effect on the hydrogen-ion concentrations of the solutions.

(3) The precipitates obtained by the interaction of a solution of sodium silicate, $Na_2O,2{\cdot}16SiO_2$, and metallic-salt solutions, except that of calcium chloride, contained less silica than that required to form the metasilicates.

(4) The hydrogen-ion concentrations at which these silicate precipitates began to form in solutions of p_H less than 7 were approximately those at which their corresponding hydroxides separate. The silicate precipitates obtained from alkaline solutions appeared

when the hydrogen-ion concentrations had not been reduced to the extent required by their respective hydroxides.

(5) The results have been discussed in relation to the question of soil acidity.

The author acknowledges his indedtedness to the Department of Scientific and Industrial Research for a personal grant, to the Chemical Society for a grant from its research fund, and to Professor J. C. Philip, F.R.S., for kindly placing facilities at his disposal.

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SOUTH KENSINGTON.
[*Received, December 8th*, 1926.]

LXV.—*The Inhibitory Effect of Substituents in Chemical Reactions. Part I. The Reactivity of the Amino-group in Substituted Arylamines.*

By GEORGE MALCOLM DYSON, HERBERT JOHN GEORGE, and ROBERT FERGUS HUNTER.

IN a study of the effect of substituents of different polar and steric character in certain organic chemical reactions, the first problem which it appeared desirable to investigate was the effect on the reactivity of the amino-group in substituted anilines; for this purpose, the reaction by which we have synthesised numerous thiocarbimides and thiocarbamides (J., 1924, **125**, 1702; *J. Soc. Chem. Ind.*, 1926, **45**, 83T; *Rec. trav. chim.*, 1926, **45**, 421) appeared well suited.

A primary amine can react with thiocarbonyl chloride to give two substances. The primary product is a thiocarbamyl chloride (equation A). This, in the presence of water, normally loses hydrogen chloride, yielding the corresponding thiocarbimide (equation B). When, however, inhibitory groups are present, the thiocarbamyl chloride loses hydrogen chloride with considerable reluctance and reacts with a second molecule of the amine to give the *s*-diarylthiocarbamide (equation C).

$$\mathrm{NH_2R + CSCl_2 = NHR{\cdot}CSCl + HCl} \quad . \quad . \quad (\text{A})$$

$$\mathrm{NHR{\cdot}CSCl \xrightarrow{H_2O} RNCS + HCl} \quad . \quad . \quad . \quad (\text{B})$$

$$\mathrm{NHR{\cdot}CSCl + NH_2R = CS(NHR)_2 + HCl} \quad . \quad . \quad . \quad (\text{C})$$

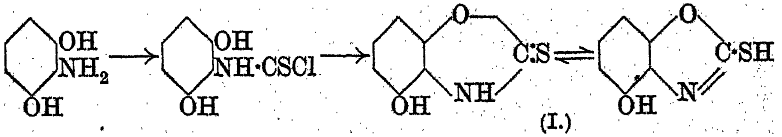
The ability of the thiocarbamyl chloride to eliminate hydrogen chloride is therefore a measure of the influence of the substituent on the reactivity of the original amine. When several inhibitory groups are present, as, for instance, in *s*-tribromoaniline and 2 : 4 : 6-trinitroaniline, inhibition of the reaction (A) may take place.

The various arylamines were treated with excess of thiocarbonyl chloride in the presence of water under standard conditions. When the amine was reactive, as in the nuclear methyl-substitution derivatives of aniline, the reaction was usually complete in 10 minutes and the thiocarbimide was isolated in 80—90% yield. When slight inhibition was present, as in the monochloroanilines (Dyson, George, and Hunter, J., 1926, 3041), thiocarbimide formation took place to the extent of about 60—70%, but the reaction was much slower, requiring about 30 minutes. When the reactivity of the amino-group was considerably depressed, as in anthranilic acid, the reaction with thiocarbonyl chloride was exceedingly slow and the only isolable product was the *s*-diarylthiocarbamide. With substances such as 2 : 6-dichloroaniline, no reaction whatever took place under these conditions; such amines were also recovered unchanged after being heated at 180° with thiocarbonyl chloride under pressure.

The experiments described in this paper are not a crucial test of the reactivity of arylamines, but are merely preliminary experiments carried out in connexion with a comprehensive study of the inhibition of organic reactions; the quantitative results will be published later.

The experiments of Dyson and Hunter (*J. Soc. Chem. Ind.*, 1926, **45**, 83T) have shown that no possible combination of nuclear methyl groups appreciably affects the reactivity of the amino-group towards thiocarbonyl chloride, the three toluidines, *o*-4-, *m*-4-, and *p*-xylidines, ψ-cumidine, mesidine, and aminopentamethylbenzene all giving nearly quantitative yields of the corresponding thiocarbimides. We have since found that *o*-3- and *m*-2-xylidines also behave normally in this respect.

The effect of a hydroxyl group in the ortho-position to the amino-group cannot be directly determined, since it reacts with the chlorine atom of the intermediate thiocarbamyl chloride with the formation of a 1-thiobenzoxazole. Its effect on the amino-group appears, however, to be slight, since 2 : 6-dihydroxyaniline reacts readily with thiocarbonyl chloride, giving 3-hydroxy-1-thiobenzoxazole (I).



(I.)

The methoxy- and the ethoxy-group also have only a slight inhibitory effect on the amino-group, since the three anisidines, 3 : 4-, 2 : 5-, and 2 : 6-dimethoxyanilines, and the three phenetidines all react normally with thiocarbonyl chloride, giving the corresponding thiocarbimides.

The effect of the cyano-group appears to lie between those of the alkyloxy-groups and the halogens, since *m*- and *p*-cyanoanilines and 2 : 5-dicyanoaniline react fairly readily, giving the corresponding cyano-substitution derivatives of phenylthiocarbimide.

Chlorine atoms considerably depress the reactivity of the amino-group in the chloroanilines; two *o*-chlorine atoms are necessary, however, for complete inhibition (Dyson, George, and Hunter, *loc. cit.*). Since the reaction becomes progressively easier with *o*-chloroaniline, *o*-bromoaniline, and *o*-iodoaniline, the effect of a halogen substituent is clearly due to a combination of both steric and polar effects. Indeed, the reaction between thiocarbonyl chloride and *o*-iodoaniline is very vigorous and is accompanied by a considerable evolution of heat (almost sufficient in our experiments to cause the supernatant water to boil). The hindering effect of an *o*-halogen atom does not appear to be affected by replacement of the second *o*-hydrogen atom by a methyl group, since 3 : 5-dibromo-*o*-toluidine reacted normally with thiocarbonyl chloride, giving 3 : 5-*dibromo*-o-*tolylthiocarbimide*, under conditions in which the isomeric 2 : 4 : 6-tribromo-*m*- and 3 : 5-dibromo-*p*-toluidines were recovered unchanged.

The effect of the nitro-group is very similar to that of the chlorine atom: *o*-, *m*-, and *p*-nitrophenylthiocarbimides were obtained from the corresponding nitroanilines with some difficulty, and complete inhibition was observed in the cases of 2 : 4- and 2 : 6-dinitroanilines and 2 : 4 : 6-trinitroaniline. On the other hand, 3 : 5-dinitroaniline reacted with thiocarbonyl chloride with difficulty, giving s-*bis*-3 : 5-*dinitrophenylthiocarbamide*. So far as we are aware, this is the first recorded instance of a 2 : 4-disubstituted benzene derivative being less reactive than the 3 : 5-isomeride. Further confirmation of the marked inhibitory effect of *o*-halogeno- and of nitro-substituents was obtained by an examination of 3-nitro-*o*-toluidine and 2-nitro-*p*-phenetidine, which reacted sluggishly with thiocarbonyl chloride, giving the corresponding thiocarbimides, and of 2 : 6-dichloro-, 2 : 6-dibromo-, and 2 : 6-di-iodo-*p*-nitroanilines, 4 : 6-dibromo-*o*-nitroaniline, and 2 : 4 : 6-tribromo-*m*-nitroaniline, with all of which complete inhibition was observed.

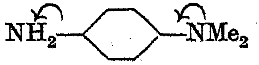
These results throw grave doubt on the theory of steric hindrance which attributes inhibition to the decrease of free space caused by the substituent (Henry, *Ber.*, 1877, **10**, 2041; Wegscheider, *Monatsh.*, 1895, **16**, 137; Angeli, *Atti R. Accad. Lincei*, 1896, **1**, 84), particularly since the molecular volumes of the methoxy- (37·1) and the methyl (25·5) group (Le Bas, "The Molecular Volumes of

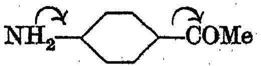
Liquid Chemical Compounds") are considerably greater than the atomic volume (22·1) of chlorine.

Finally the effects of acidic and basic groups were studied. The sulpho- and the carboxyl group both exert strong inhibitory actions, the former being the more powerful, since sulphanilic acid could not be induced to react with thiocarbonyl chloride, whereas anthranilic acid was very slowly converted into s-*di*-o-*carboxyphenylthiocarbamide.*

The experiments of Billeter and Steiner (*Ber.*, 1887, **20**, 228) indicate that there is no appreciable steric hindrance due to the amino-groups in the phenylenediamines. Acylation of one amino-group, however, depresses the reactivity of the other, since s-*di*-p-*acetamidophenylthiocarbamide* is the only product isolable from *p*-aminoacetanilide and thiocarbonyl chloride and is only formed very slowly in the presence of water at 100°. Alkylation has little effect on the amino-group, since *as*-dimethyl-*p*-phenylenediamine readily passes into p-*dimethylaminophenylthiocarbimide* under the usual conditions. This would appear to be explicable on the "electron sink" properties of the carbonyl group (Allan, Oxford, Robinson, and Smith, J., 1926, 401), in which case the effect would be expected to be still more strikingly manifested in *p*-aminoacetophenone as shown in the formulæ (II) and (III).

(II.)





(III.)

p-Aminoacetophenone, however, reacts with thiocarbonyl chloride under the usual conditions with the greatest ease, giving a 70% yield of the corresponding thiocarbimide.

A point of interest in connexion with the organoleptic properties of thiocarbimides is that the *o*-substituted derivatives usually have an unpleasant pungent odour, whereas the *p*-substituted derivatives are invariably associated with the pleasant odour of aniseed.

EXPERIMENTAL.

Rapid Thiocarbimide Formation.

The thiocarbimides described below were usually obtained as follows: Thiocarbonyl chloride (1·3 mols.) was completely suspended in water (10 vols.) at 15° by vigorous stirring during the addition of a solution of the arylamine (1 mol.) in chloroform (5 vols.). After 15 minutes' stirring, the chloroform layer was removed and dried with calcium chloride, and the solvent and the excess of thiocarbonyl chloride were distilled off on a steam-bath. The thiocarbimide was obtained either by fractionating (under reduced or atmospheric pressure according to the nature of the compound) or by steam-distilling the residue.

The arylthiocarbamides, NHAr·CS·NH_2, were prepared from the respective thiocarbimides and warm alcoholic ammonia, and the *s*-diarylthiocarbamides, $CS(NHAr)_2$, by condensing the thiocarbimides (1 mol.) with the corresponding arylamines (1 mol.) in alcohol.

m-*Xylyl-2-thiocarbimide* was obtained from *m*-2-xylidine by fractionation of the residue after removal of the solvent and the excess of thiocarbonyl chloride, and distilled as a colourless oil, b. p. 247°/760 mm. (Found : S, 19·8. C_9H_9NS requires S, 19·6%). m-*Xylyl-2-thiocarbamide* crystallised from alcohol in minute, square prisms, m. p. 190° (Found : S, 19·0. $C_9H_{12}N_2S$ requires S, 18·8%). s-*Di*-m-*xylyl-2-thiocarbamide* crystallised in glistening, flat plates, m. p. 208° (Found : S, 11·4. $C_{17}H_{20}N_2S$ requires S, 11·3%).

o-*Xylyl-3-thiocarbimide* was obtained from *o*-3-xylidine (0·75 g.) and isolated by microdistillation as a colourless oil of pungent odour, b. p. 262—263°/760 mm. (yield, 0·8 g.). o-*Xylyl-3-thiocarbamide* crystallised from alcohol in brilliant, white needles, m. p. 182° (Found : S, 18·5%).

o-*Anisylthiocarbimide* was obtained from *o*-anisidine, and distilled as a pale yellow oil of unpleasant odour, b. p. 266—267°/760 mm. (Found : S, 19·2. C_8H_7ONS requires S, 19·4%). o-*Anisylthiocarbamide* crystallised in white needles, m. p. 148—149° (Found : S, 17·2. $C_8H_{10}ON_2S$ requires S, 17·6%). s-*Di*-o-*anisylthiocarbamide* formed glistening prisms, m. p. 134° (Found : S, 11·0. $C_{15}H_{16}O_2N_2S$ requires S, 11·1%).

m-*Anisylthiocarbimide* was prepared from *m*-anisidine and distilled as a colourless oil of pungent odour, b. p. 267°/760 mm. (Found : S, 19·3%). m-*Anisylthiocarbamide* crystallised in glistening prisms, m. p. 160° (Found : S, 17·0%). s-*Di*-m-*anisylthiocarbamide* separated from alcohol in clear, crystalline plates, m. p. 126° (Found : S, 13·2%).

p-Anisylthiocarbimide is a pale yellow oil having a pleasant odour of aniseed, b. p. 280—281°/760 mm. *p*-Anisylthiocarbamide forms small prisms, m. p. 211°, and *s*-di-*p*-anisylthiocarbamide, small, glistening plates, m. p. 187°.

2 : 5-Dimethoxyaniline was most conveniently prepared as follows : A solution of quinol (20 g.) in 35% potassium hydroxide was treated with 50 c.c. of methyl sulphate, giving 24 g. of *p*-dimethoxybenzene, m. p. 56° ; this was converted into 2 : 5-dimethoxynitrobenzene by nitration with nitric acid (*d* 1·2) in glacial acetic acid, and the nitro-derivative reduced with tin and hydrochloric acid. The dimethoxyaniline, isolated by means of ether, separated from dilute alcohol in small crystals, m. p. 84° (Magatti, *Ber.*, 1881,

14, 71; Baessler, *Ber.*, 1884, **17**, 2119). The compound rapidly turned red on exposure to the atmosphere.

2 : 5-*Dimethoxyphenylthiocarbimide.*—The dark-coloured mixture obtained on addition of the dimethoxyaniline (8 g.) to thiocarbonyl chloride in water was steam-distilled, and the distillate extracted with chloroform, yielding the thiocarbimide in large crystals, m. p. 32° (to an oil of pungent odour). 2 : 5-*Dimethoxyphenylthiocarbamide* forms small crystals, m. p. 161°, from alcohol (Found: S, 15·3. $C_9H_{12}O_2N_2S$ requires S, 15·1%). s-*Bis*-2 : 5-*dimethoxyphenylthiocarbamide* forms small crystals, m. p. 127° (Found: S, 9·3. $C_{17}H_{20}O_4N_2S$ requires S, 9·2%).

3 : 4-*Dimethoxyphenylthiocarbimide* was obtained from 3 : 4-dimethoxyaniline (prepared from 4-nitroveratrole) as an oil of pungent odour similar to that of phenylthiocarbimide; it could not be crystallised (Found: S, 17·0. $C_9H_9O_2NS$ requires S, 16·4%). 3 : 4-*Dimethoxyphenylthiocarbamide* separated from alcohol as a microcrystalline powder, m. p. 234° (Found: S, 15·0%). s-*Bis*-3 : 4-*dimethoxyphenylthiocarbamide* formed white prisms, m. p. 140°.

o-*Ethoxyphenylthiocarbimide* was obtained from *o*-phenetidine, as a pale yellow oil, b. p. 273—275°/760 mm. (Found: S, 18·0. C_9H_9ONS requires S, 17·9%). o-*Ethoxyphenylthiocarbamide* crystallised from dilute alcohol in small crystals, m. p. 126° (Found: S, 16·5. $C_9H_{12}ON_2S$ requires S, 16·3%). s-*Di*-o-*ethoxyphenylthiocarbamide*, after three recrystallisations from dilute alcohol, formed large prisms, m. p. 125° (Found: S, 10·0. $C_{17}H_{20}O_2N_2S$ requires S, 10·2%).

m-*Ethoxyphenylthiocarbimide* was obtained from *m*-phenetidine as a clear, colourless oil of pungent odour, b. p. 278°/758 mm. (Found: S, 17·8%). m-*Ethoxyphenylthiocarbamide* formed short, white prisms, m. p. 167° (Found: S, 16·6%). s-*Di*-m-*ethoxyphenylthiocarbamide* separated from alcohol in aggregates of coarse needles, m. p. 115° (Found: S, 10·0%).

p-Ethoxyphenylthiocarbimide forms large, glistening plates having the odour of aniseed, m. p. 76°. *p*-Ethoxyphenylthiocarbamide forms small crystals, m. p. 176°, and *s*-di-*p*-ethoxyphenylthiocarbamide, plates, m. p. 171°.

o-*Carbethoxyphenylthiocarbimide.*—The rate of addition of ethyl anthranilate solution in chloroform to the thiocarbonyl chloride suspension was adjusted so that the temperature did not rise above 30°. The thiocarbimide distilled under reduced pressure as a pale, thick oil of nauseating odour, b. p. 150—151°/1 mm. (Found: S, 15·0. Calc. for $C_{10}H_9O_2NS$: S, 15·4%). *o*-Carbethoxyphenylthiocarbamide separated from 50% alcohol in needles, m. p. 300—305° (Found: S, 14·2. Calc. for $C_{10}H_{12}O_2N_2S$: S, 14·3%).

s-Di-*o*-carbethoxyphenylthiocarbamide crystallised slowly from its solutions in colourless prisms which decomposed without melting (Found: S, 8·0. Calc. for $C_{19}H_{20}O_4N_2S$: S, 8·6%).

m-*Carbethoxyphenylthiocarbimide* distilled as a pale yellow oil, b. p. 152°/10 mm. (Found: S, 15·2%). m-*Carbethoxyphenylthiocarbamide* formed long, glistening prisms, m. p. 294—295° (Found: S, 14·2%). s-*Di*-m-*carbethoxyphenylthiocarbamide* separated from alcohol in white prisms which decomposed without melting (Found: S, 8·0%). This compound was sometimes difficult to crystallise.

p-*Carbethoxyphenylthiocarbimide* crystallised from dilute alcohol in glistening plates having an odour of aniseed, m. p. 58° (Found: S, 15·3%). p-*Carbethoxyphenylthiocarbamide* formed glistening needles, m. p. 159° (Found: S, 14·0%). s-*Di*-p-*carbethoxyphenylthiocarbamide* crystallised in small prisms, m. p. 165° (Found: S, 9·0%).

p-*Dimethylaminophenylthiocarbimide* was prepared from *as*-dimethyl-*p*-phenylenediamine and thiocarbonyl chloride in the usual way; after removal of the chloroform on a steam-bath, the residue was steam-distilled for 8—10 hours, the thiocarbimide slowly passing over as an oil which solidified in pale yellow prisms, m. p. 67° (Found: S, 18·2. $C_9H_{10}N_2S$ requires S, 17·9%). p-*Dimethylaminophenylthiocarbamide* formed pale yellow prisms, m. p. 190° (Found: S, 16·0. $C_9H_{13}N_3S$ requires S, 16·4%).

p-*Acetylphenylthiocarbimide* was prepared from *p*-aminoacetophenone in the same way as the dimethylaminophenyl compound, and distilled slowly in steam as a solid of pronounced aniseed odour. It crystallised in broad plates (yield, 70%), m. p. 76° (Found: S, 18·0. C_9H_7ONS requires S, 18·1%). p-*Acetylphenylthiocarbamide* formed small, yellow prisms, m. p. 215° (decomp.) (Found: S, 16·8. $C_9H_{10}ON_2S$ requires S, 16·5%). s-*Di*-p-*acetylphenylthiocarbamide* crystallised in sparingly soluble, microscopic crystals, m. p. 198° (Found: S, 10·0. $C_{17}H_{16}O_2N_2S$ requires S, 10·8%).

Retarded Thiocarbimide Formation.

In the preparation of the thiocarbimides described below, the mixture was stirred for 30 minutes after the addition of the solution of the amine.

m-Nitrobenzonitrile (m. p. 116°; prepared by the nitration of benzonitrile) (14 g.) was warmed with tin (40 g.) and concentrated hydrochloric acid (100 c.c.), the reaction mixture treated with excess of 20% sodium hydroxide, and *m*-cyanoaniline extracted with ether; after recrystallisation from alcohol, this had m. p. 52°.

m-*Cyanophenylthiocarbimide* was obtained as an oil of pungent odour which decomposed on heating to 250°. m-*Cyanophenylthiocarbamide* crystallised in long needles, m. p. 137° (Found: S, 18·0. $C_8H_7N_3S$ requires S, 18·0%). s-*Di*-m-*cyanophenylthiocarbamide* separated from alcohol in small, cream-coloured crystals, m. p. 144° (Found: S, 11·0. $C_{15}H_{10}N_4S$ requires S, 11·5%).

p-*Cyanophenylthiocarbimide* was obtained by steam-distilling the residue obtained after removal of the chloroform and the excess of thiocarbonyl chloride; on recrystallisation from dilute alcohol it formed glistening, fibrous needles having a strong odour of aniseed, m. p. 45° (Found: S, 19·6. $C_8H_4N_2S$ requires S, 20·0%).

p-*Cyanophenylthiocarbamide* separated from dilute alcohol in prisms, m. p. 169° (Found: S, 18·2%). s-*Di*-p-*cyanophenylthiocarbamide* formed white crystals, m. p. 171° (Found: S, 11·6%).

2 : 5-Dicyanoaniline was prepared as follows: *p*-Dicyanobenzene (prepared from *p*-cyanoaniline by the Sandmeyer reaction) (25 g.) was nitrated with nitric acid (*d* 1·5) at 80° for 20 minutes; a considerable portion of the material was oxidised to benzoquinone. On pouring the nitration product into cold water and extracting the product with ligroin (in which benzoquinone is almost insoluble), 5 g. of the required 2 : 5-dicyanonitrobenzene were obtained, which, on reduction with tin and hydrochloric acid, yielded the dicyanoaniline. On recrystallisation, the amine formed small, brown crystals, m. p. 62°. The yield was 1·5 g.

2 : 5-*Dicyanophenylthiocarbimide*, after recrystallisation from alcohol, retained a strong almond-like odour; it decomposed without melting (Found: S, 17·4. $C_9H_3N_3S$ requires S, 17·3%). 2 : 5-*Dicyanophenylthiocarbamide* separated from alcohol in needles, m. p. 228°.

o-*Bromophenylthiocarbimide* distilled as a colourless oil of pungent odour, b. p. 257°/770 mm. o-*Bromophenylthiocarbamide* separated from alcohol in rosettes of glistening, rhombic prisms, m. p. 125° (Found: S, 14·0. $C_7H_7N_2BrS$ requires S, 13·9%). s-*Di*-o-*bromophenylthiocarbamide* formed long needles, m. p. 157° (Found: S, 9·0. $C_{13}H_{10}N_2Br_2S$ requires S, 8·3%).

2 : 5-*Dibromophenylthiocarbimide* was obtained from 2 : 5-dibromoaniline as a clear oil, b. p. 240°, which formed a glacial mass of needles on cooling; m. p. 17—18° (Found: S, 11·2. $C_7H_3NBr_2S$ requires S, 10·9%). 2 : 5-*Dibromophenylthiocarbamide* formed long needles, m. p. 130° (Found: S, 10·5. $C_7H_6N_2Br_2S$ requires S, 10·3%). s-*Di*-2 : 5-*dibromophenylthiocarbamide*, after two recrystallisations from dilute alcohol, had m. p. 154° (Found: S, 6·0. $C_{13}H_8N_2Br_4S$ requires S, 5·9%).

o-*Iodophenylthiocarbimide* formed long, slender needles having a pungent odour, m. p. 39°. o-*Iodophenylthiocarbamide* separated from alcohol in broad plates, m. p. 157° (Found: S, 11·0. $C_7H_7N_2IS$ requires S, 11·5%). s-*Di*-o-*iodophenylthiocarbamide* separated from dilute alcohol in small, ill-defined crystals, m. p. 164° (decomp.).

m-*Iodophenylthiocarbimide* formed glistening needles, m. p. 46° (Found: S, 12·4. C_7H_4NIS requires S, 12·2%). m-*Iodophenylthiocarbamide* crystallised in white needles, m. p. 160° (decomp.) (Found: S, 11·8%).

3 : 5-*Dibromo*-o-*tolylthiocarbimide*.—The dibromotoluidine (10 g.) was shaken with water and thiocarbonyl chloride, and the mixture steam-distilled; the thiocarbimide was then obtained as a white solid of pungent odour. On recrystallisation from dilute alcohol, it formed a pasty mass of crystals, m. p. about 25°, b. p. 280° (Found: S, 10·0. $C_8H_5NBr_2S$ requires S, 10·5%).

3-*Nitro*-o-*tolylthiocarbimide*.—3-Nitro-*o*-toluidine (10 g.) was refluxed with thiocarbonyl chloride (10 g.) for 10 minutes, and the excess of thiocarbonyl chloride removed in steam. The residue, on recrystallisation from glacial acetic acid, yielded the thiocarbimide in lemon-yellow plates, m. p. 69° (Found: S, 16·1. $C_8H_6O_2N_2S$ requires S, 16·5%).

2-*Nitro*-4-*ethoxyphenylthiocarbimide*.—Ten g. of 2-nitro-*p*-phenetidine were gradually added to a suspension of thiocarbonyl chloride (10 g.) in water (300 c.c.). The thiocarbimide, isolated in the same way as the nitrotolyl compound, crystallised from glacial acetic acid in flat, orange plates, m. p. 78° (Found: S, 14·4. $C_9H_8O_3N_2S$ requires S, 14·3%). 2-*Nitro*-4-*ethoxyphenylthiocarbamide* separated from alcohol in glistening, orange-brown crystals, m. p. 177° (Found: S, 13·0. $C_9H_{11}O_3N_3S$ requires S, 13·3%).

Thiocarbamide Formation.

s-*Bis*-3 : 5-*dinitrophenylthiocarbamide*.—3 : 5-Dinitroaniline (10 g.) was shaken with thiocarbonyl chloride (11 g.) in water (150 c.c.) for ½ hour and the excess of thiocarbonyl chloride was then removed in steam. The residue, after several recrystallisations from light petroleum–acetic acid, gave the thiocarbamide in minute, yellow prisms, m. p. 160° (Found: S, 7·5. $C_{13}H_8O_8N_6S$ requires S, 7·8%).

s-*Di*-o-*carboxyphenylthiocarbamide*.—Anthranilic acid (50 g.) was refluxed with thiocarbonyl chloride (50 g.) and water (300 c.c.) for 42 hours, and the excess of chloride removed by steam distillation. The residue was extracted with a large volume of alcohol; the thiocarbamide was then obtained as a granular powder. After several recrystallisations from alcohol (animal charcoal) it was obtained in small crystals, m. p. 300° (decomp.) (Found: S, 10·0. $C_{15}H_{12}O_4N_2S$ requires S, 10·1%).

s-*Di*-p-*acetamidophenylthiocarbamide* was obtained from *p*-aminoacetanilide (20 g.) in the same way as the dicarboxyphenylthiocarbamide, and crystallised in small prisms, m. p. 220° (decomp.) (Found: S, 8·8. $C_{17}H_{18}O_2N_4S$ requires S, 9·3%).

Inhibition.

2 : 6-Dichloro-, -dibromo-, -di-iodo-*p*-nitroanilines, 4 : 6-dibromo-*o*-nitroaniline, and 2 : 4 : 6-tribromo-*m*-nitroaniline were all prepared by the methods given in the literature; they were recovered unchanged after treatment with thiocarbonyl chloride and water and identified by m. p. and mixed m. p. determinations. Sulphanilic acid was recovered unchanged after being refluxed with excess of thiocarbonyl chloride and water for 3 hours and identified by its properties, analysis (Found: S, 18·6%), and by the formation of Orange II on diazotisation and coupling with β-naphthol.

In conclusion, we wish to express our gratitude to Professors J. F. Thorpe, F.R.S., and C. K. Ingold, F.R.S., for the interest they have taken in this work and to the Ramsay Memorial Fellowship Trust for a Fellowship awarded to one of us (R. F. H.). Part of the expense has been defrayed by grants from the Research Fund of the Chemical Society and the Dixon Fund of the University of London.

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[*Received, October 22nd*, 1926.]

LXVI.—*Studies on the Walden Inversion. Part XI. Evidence for the Bivalency of Carbon from Some Reactions of α-Chloroethylbenzene. αα'-Diphenyldiethyl Ether.*

By ALLAN MILES WARD.

THE experiments here described were undertaken as a continuation of the method of Part X of this series (J., 1926, 1184) in order to obtain fuller information on the mechanism of the replacement of the halogen in α-chloroethylbenzene; the course of replacement was accordingly followed both by titration and by change of rotation.

The interconversion of the phenylmethylcarbinols was first demonstrated by McKenzie and Clough (J., 1913, **103**, 687); their results may be summarised by the following scheme:

$$\begin{tikzcd}
d\text{-CHPhMe}\cdot\text{OH} \arrow[r, "SOCl_2"] \arrow[d, shift left, "PCl_5"] & d\text{-CHPhMeCl} \arrow[d, shift left, "\begin{array}{l}Ag_2O + water\\ NaOH + water\end{array}"] \\
l\text{-CHPhMeCl} \arrow[u, shift left, "\begin{array}{r}Ag_2O + water\\ NaOH + water\end{array}"] & l\text{-CHPhMe}\cdot\text{OH} \arrow[l, "SOCl_2"'] \arrow[u, shift left, "PCl_5"]
\end{tikzcd}$$

Phosphorus trichloride thus behaves like hydrogen chloride towards phenylmethylcarbinol (compare Pickard and Kenyon, J., 1911, **99**, 71), whilst thionyl chloride behaves differently. In each of the above reactions, with the exception of that of thionyl chloride, racemisation is very considerable.

The displacement of the halogen in α-chloroethylbenzene is here studied in aqueous (20% by volume) ethyl-alcoholic solution at 28·7° and at 50·0°, both alone and also in the presence of sodium hydroxide. The products of reaction in each case are α-phenyldiethyl ether and phenylmethylcarbinol, so that the course of the reaction may be represented thus:

$$\text{(I.)}\quad \mathrm{CHPhMeCl + EtOH \longrightarrow CHPhMe{\cdot}OEt + HCl.}$$

$$\text{(II.)}\quad \mathrm{CHPhMeCl + H_2O \longrightarrow CHPhMe{\cdot}OH + HCl.}$$

The most interesting aspect of these reactions is, however, that the displacement of the halogen proceeds at the same speed whether sodium hydroxide is present in or absent from the solution, and in all cases the velocity coefficients for the reactions, calculated on the basis of a unimolecular reaction, are in good agreement, as shown by the following collected data.

r-α-Chloroethylbenzene (approx. *N*/10).
Solvent: Aqueous (20% by volume) ethyl alcohol.

Exper.	Temp.	Conditions.	*k*.
3	28·7°	Alone	0·0560
4	28·7	NaOH (approx. *N*/10)	0·0561
5	28·7	NaOH (approx. *N*/5)	0·0560
6	50·0	Alone	0·589
7	50·0	NaOH (approx. *N*/10)	0·590
8	50·0	NaOH (approx. *N*/5)	0·590

The temperature coefficient for 10° is thus 3·02.

These results are analogous to those obtained by Senter (J., 1915, **107**, 908) for the displacement of the halogen in phenylchloroacetic acid in aqueous solution, and for the sodium salt in aqueous and also in sodium hydroxide solutions, where it was found that the displacement reaction in each case is one and the same, namely, the reaction between water and the phenylchloroacetate ion. Results of a similar nature were obtained by Senter and Tucker (J., 1916, **109**, 690) for phenylbromoacetic acid, and they considered that in addition to the reaction

$$\mathrm{CHPhBr{\cdot}CO_2' + H_2O\ (excess) \longrightarrow CHPh(OH){\cdot}CO_2' + HBr,}$$

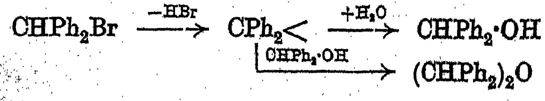
water reacted with the undissociated acid also, but about 120 times more slowly. In the present case equations I and II would represent the reactions from the kinetic point of view, but, just as for the reactions between water and the phenylchloroacetate and phenylbromoacetate ions, they fail to provide an explanation for the non-intervention of sodium hydroxide in these reactions.

The velocities of replacement of the halogen in *d*-α-chloroethylbenzene in aqueous ethyl-alcoholic solution in the presence and the absence of sodium hydroxide were also measured by determining the changes in the rotations of the solutions with time at 28·6°. The total change in the rotations of the solutions was small, so that the experimental error is of sufficient relative magnitude to introduce considerable variation in the velocity coefficients when calculated on the basis of a unimolecular reaction according to the formula $k = 2{\cdot}3/t \,.\, \log_{10}\{(\theta_0 - \theta_\infty)/(\theta_t - \theta_\infty)\}$. The mean of the coefficients in aqueous ethyl alcohol alone is 0·0608, whilst in the presence of sodium hydroxide the mean obtained is 0·0558. These experiments at least confirm the results derived from the titration experiments, namely, that sodium hydroxide is playing no part in the displacement of the halogen.

The displacement of the halogen in β-chloroethylbenzene is in quite striking contrast with the above. Under similar conditions to those employed for α-chloroethylbenzene, the displacement in aqueous alcohol was negligible, whilst in the presence of sodium hydroxide, velocity coefficients agreeing with a bimolecular reaction were obtained; also the displacement of the halogen takes place very much more slowly from β-chloroethylbenzene than from α-chloroethylbenzene. Sodium hydroxide or its ions are therefore playing some essential part in the elimination of the halogen from β-chloroethylbenzene. In other reactions recorded, α- and β-chloroethylbenzenes behave very differently. Thus alcoholic potassium cyanide, followed by hydrolysis, yields β-phenylpropionic acid from β-chloroethylbenzene (Fittig and Kiesow, *Annalen*, 1870, **156**, 245; Schramm, *Monatsh.*, 1887, **8**, 101; Fischer and Schmitz, *Ber.*, 1906, **39**, 2208), whilst from α-chloroethylbenzene under similar conditions α-phenyldiethyl ether is obtained. This ether was first prepared by Thorpe (*Proc. Roy. Soc.*, 1869, **18**, 123) by the interaction of α-bromoethylbenzene and a saturated solution of ammonia in ethyl alcohol, no α-phenylethylamine being produced; it formed also the main product of the reaction between potassium acetate and α-bromoethylbenzene in ethyl-alcoholic solution. The mechanism of the displacement of the halogen from α-chloroethylbenzene would thus appear to be quite different from that in the case of β-chloroethylbenzene.

It was found also in the present experiments that the replacement of the halogen in α-chloroethylbenzene at 50° gives phenylmethylcarbinol only; at 100°, however, the products consist of styrene, phenylmethylcarbinol and αα′-diphenyldiethyl ether; if the boiling is continued for but 5 minutes, an appreciable amount of the ether is formed. $\alpha\alpha'$-Diphenyldiethyl ether has previously been prepared, together with phenylmethylcarbinol, by Oddo (*Gazzetta*, 1907, **37**, ii, 360) by the interaction of magnesium methyl iodide and benzaldehyde in the presence of pyridine. Marshall (J., 1914, **105**, 530), in the course of his investigation on the interaction of magnesium methyl iodide and benzaldehyde, obtained a substance which he considered to be $\alpha\alpha'$-diphenyldiethyl ether, since it did not react with sodium and gave α-chloroethylbenzene on reaction with phosphorus pentachloride. More recently, Wuyts (*Bull. Soc. chim. Belg.*, 1921, **30**, 30), in studying the optical activation of *r*-phenylmethylcarbinol by means of camphorsulphonic acid, found the predominant reaction to be the formation of *l*-$\alpha\alpha'$-diphenyldiethyl ether with $\alpha_{\mathrm{D}}^{23^\circ} - 1{\cdot}11^\circ$. Descamps (*ibid.*, 1924, **33**, 139) has extended this investigation on the "catalytic dehydration" of phenylmethylcarbinol to $\alpha\alpha'$-diphenyldiethyl ether. In view of the present results that this ether may be produced readily in the presence of water from α-chloroethylbenzene, and also from phenylmethylcarbinol by boiling with dilute hydrochloric acid, it does not appear justifiable to consider this reaction to be due to a direct dehydration between two molecules of phenylmethylcarbinol.

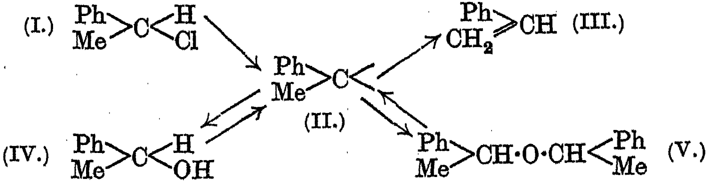
The only similar example of ether formation known to the author is the case of benzhydrol and diphenylbromomethane. Friedel and Balsohn (*Bull. Soc. chim.*, 1880, **33**, 339) found that diphenylbromomethane, on boiling with water, yielded mainly *s*-tetraphenyldimethyl ether together with a small amount of benzhydrol. This ether had previously been prepared by Linnemann (*Annalen*, 1865, **133**, 14) by prolonged heating of benzhydrol at its boiling point (compare also Thörner and Zincke, *Ber.*, 1878, **11**, 1398; Nef, *Annalen*, 1897, **298**, 234). Nef (*loc. cit.*) found that the displacement of the halogen in diphenylbromomethane by means of water at room temperature gave benzhydrol only, but that *s*-tetraphenyldimethyl ether alone resulted when boiling water was used, and to explain this he assumed that the reactions proceed through a stage involving bivalent carbon by the following mechanism :



$$\begin{tikzcd} CHPh_2Br \arrow[r, "-HBr"] & CPh_2< \arrow[r, "+H_2O"] \arrow[dr, "CHPh_2\cdot OH"'] & CHPh_2\cdot OH \\ & & (CHPh_2)_2O \end{tikzcd}$$

the addition reactions being exactly analogous to those shown by the isonitriles and the halogenated acetylenes (compare Nef, *Annalen*, 1892, **270**, 267; 1894, **280**, 291; 1895, **287**, 265; 1897, **298**, 202; Lawrie, *Amer. Chem. J.*, 1906, **36**, 489).

In a similar way, the reaction products from α-chloroethylbenzene may be explained by the following scheme :



the first stage of the reaction being the elimination of hydrogen chloride from (I) to yield the highly reactive intermediate phase (II), which then (*a*) undergoes irreversible isomeric change to give styrene (III), (*b*) adds water to give phenylmethylcarbinol (IV), (*c*) adds phenylmethylcarbinol to give αα′-diphenyldiethyl ether (V). The scheme also agrees with the observation that phenylmethylcarbinol, on boiling with *N*/2-hydrochloric acid for 8 hours, yields a mixture of (III), (IV), and (V), and accounts for the similar behaviour of αα′-diphenyldiethyl ether on boiling with *N*/2-hydrochloric acid.

The formation of an intermediate phase involving bivalent carbon is also in accord with the apparent non-intervention of sodium hydroxide as shown in the kinetic results for α-chloroethylbenzene, for if the reaction proceeds by the following stages,

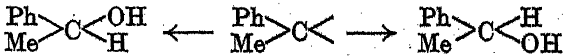
$$\text{(1) CHPhMeCl} \longrightarrow \text{CPhMe}< + \text{HCl (slow)}$$

$$\text{(2) CPhMe}< + \underset{\text{(excess)}}{H_2O} \longrightarrow \text{CHPhMe·OH (rapid)}$$

$$\text{(3) CPhMe}< + \underset{\text{(excess)}}{\text{EtOH}} \longrightarrow \text{CHPhMe·OEt (rapid)}$$

then velocity coefficients agreeing with a unimolecular reaction in accordance with stage (1) should be obtained. Further, sodium hydroxide would be expected to play no part in this transformation, for it would be without effect on stage (1), and even should it unite with CPhMe<, such a combination could be only transitory under the conditions of experiment and would lead to the same products as in (2) and (3), and this reaction would be expected to proceed with a velocity comparable with those of (2) and (3). Also by assuming the intermediate phase CPhMe<, the formation of α-phenyldiethyl ether by the reaction between α-chloroethylbenzene and alcoholic ammonia, potassium cyanide or potassium acetate is more readily understood.

The foregoing evidence is thus in accordance with the reaction proceeding through the phase CPhMe<, and it is conceivable that the addition of water to this phase may take place in two ways thus,



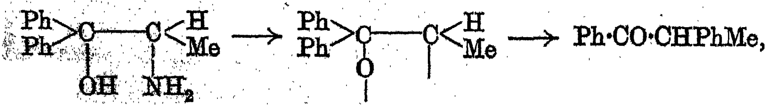
$$\begin{matrix}\text{Ph}\\ \text{Me}\end{matrix}\!>\!C\!<\!\begin{matrix}\text{OH}\\ \text{H}\end{matrix} \longleftarrow \begin{matrix}\text{Ph}\\ \text{Me}\end{matrix}\!>\!C\!< \longrightarrow \begin{matrix}\text{Ph}\\ \text{Me}\end{matrix}\!>\!C\!<\!\begin{matrix}\text{H}\\ \text{OH}\end{matrix}$$

to give rise to a mixture of *d*- and *l*-phenylmethylcarbinols. In general, this may be stated that CR_1R_2 will react with a substance XY to give a mixture of $CR_1R_2(X)Y$ and $CR_1R_2(Y)X$, the relative amounts of each isomeride produced depending on the experimental conditions. Nef (*Annalen*, 1904, **335**, 241) has employed this methylene theory to account for the racemisation of hydroxy- and halogen acids and esters of the type $CHRX{\cdot}CO_2H$, and also for the autoracemisation of the halogenosuccinic esters (see Walden, "Optische Umkehrerscheinungen," 1919, V Kapitel), by assuming that the racemisation is due to an equilibrium as follows :

$$CHR(X){\cdot}CO_2H \rightleftharpoons CR(CO_2H)\!< + HX \rightleftharpoons C(H)RX{\cdot}CO_2H.$$

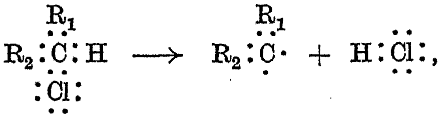
In a further discussion of these views (*J. Amer. Chem. Soc.*, 1908, **30**, 645), Nef concludes that the four valency units of carbon cannot be regarded as identical, but does not enter into a discussion of the problem of the Walden inversion in connexion with his theory, as he regards the reactions dealt with under this subject as being abnormal in character. Walden (*op. cit.*, p. 182) considers that Nef's views on autoracemisation cannot be correct, since the halogenosuccinic esters, both alone and in solution, are non-electrolytes, and that, were any free halogen acid present, then the conductivity would be appreciable; also no reaction for bromine ion is obtained with silver nitrate solution. The autoracemisation observed by Walden was, however, extremely slow, extending over many years, so that the amount of methylene phase necessary in accordance with Nef's theory must be assumed extremely small.

It might be argued that if the reaction proceeded through an unsaturated phase $CR_1R_2\!<$, then the resulting compound would of necessity be racemic in nature. There is, however, so far as the author is aware, no experimental evidence to support the view that complete racemisation would ensue. The results of McKenzie, Roger, and Wills (J., 1926, 779) on the reaction between nitrous acid and *l*-β-amino-αα-diphenyl-*n*-propyl alcohol, whereby *d*-methyldeoxybenzoin with $[\alpha]_D^{17^\circ}$ + 158° is produced although the reaction is assumed to proceed through a phase in which but three groups are attached to the centre of asymmetry according to the scheme



$$\begin{matrix}Ph\\Ph\end{matrix}\!>\!\underset{OH}{\overset{}{C}}\!-\!\!\!-\!\underset{NH_2}{C}\!<\!\begin{matrix}H\\Me\end{matrix} \longrightarrow \begin{matrix}Ph\\Ph\end{matrix}\!>\!\underset{\underset{|}{O}}{C}\!-\!\!\!-\!\underset{|}{C}\!<\!\begin{matrix}H\\Me\end{matrix} \longrightarrow Ph{\cdot}CO{\cdot}CHPhMe,$$

furnish evidence somewhat analogous to the present that optically active compounds may be produced through a phase in which less than four groups are attached at least momentarily to the centre of asymmetry. Phillips (J., 1925, **127**, 2567) had previously discussed the possible free existence of the system $+\,\mathrm{C}\begin{smallmatrix}\diagup R_1\\ -R_2\\ \diagdown R_3\end{smallmatrix}$ in an optically active state in connexion with the problem of the Walden inversion. He considers that such inversions are intimately connected with the withdrawal of two electrons from the valency shell of the atom usually designated as asymmetric; this conception is quite in accord with the mechanism now discussed, for on the basis of the Lewis–Langmuir models the reaction would be represented



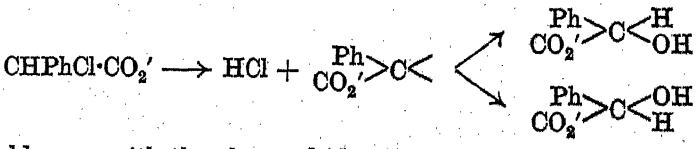
$$R_2\!:\!\overset{R_1}{\underset{:\mathrm{Cl}:}{\ddot{\underset{\cdot\cdot}{\mathrm{C}}}}}\!:\!\mathrm{H} \longrightarrow R_2\!:\!\overset{R_1}{\ddot{\underset{\cdot}{\mathrm{C}}}}\cdot + \mathrm{H}\!:\!\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\!:,$$

two electrons being withdrawn from the shell of the asymmetric carbon atom as the first stage (slow) of the reaction, to be followed by the addition reactions (rapid).

The kinetic results on the replacement of the halogen in phenylchloroacetic acid and phenylbromoacetic acid (*loc. cit.*) show the mechanisms of the halogen replacements in these cases to be exactly the same as for α-chloroethylbenzene, so that they would be represented thus:

(1) $\mathrm{CHPhX{\cdot}CO_2{}'} \longrightarrow \mathrm{CPh(CO_2{}')} + \mathrm{HX}$.
(2) $\mathrm{CPh(CO_2{}')} + \mathrm{H_2O}$ (excess) $\longrightarrow \mathrm{CHPh(CO_2{}'){\cdot}OH}$.

Further, the reaction between water and the *l*-phenylchloroacetate or *l*-phenylbromoacetate ions gives rise to a mixture of *l*- and *d*-mandelic acids, the *l*-acid being in slight excess over the *d*-acid in the case of *l*-phenylchloroacetic acid (McKenzie and Clough, J., 1908, **93**, 811; 1909, **95**, 777), whilst for *l*-phenylbromoacetic acid the reverse holds (McKenzie and Walker, J., 1916, **109**, 1685; Ward, J., 1926, 1190). The mechanisms of the reactions by which the *d*- and *l*-mandelic acids are produced cannot be differentiated (Ward, *loc. cit.*), that is, the mechanisms of the "normal" and "abnormal" reactions are identical from the ordinary kinetic point of view. The production of the mandelic acids by the addition of water in two ways to the intermediate phase, according to the scheme



$$\mathrm{CHPhCl{\cdot}CO_2{}'} \longrightarrow \mathrm{HCl} + {}^{\mathrm{Ph}}_{\mathrm{CO_2{}'}}\!\!>\!\mathrm{C}\!< \begin{array}{l} \nearrow\ {}^{\mathrm{Ph}}_{\mathrm{CO_2{}'}}\!\!>\!\mathrm{C}\!<^{\mathrm{H}}_{\mathrm{OH}} \\ \searrow\ {}^{\mathrm{Ph}}_{\mathrm{CO_2{}'}}\!\!>\!\mathrm{C}\!<^{\mathrm{OH}}_{\mathrm{H}} \end{array}$$

would agree with the observed identity of the two reactions. The similar production of phenylaminoacetic acids of either sign from a given initial phenylchloroacetic or phenylbromoacetic acid according to the solvent medium used (Senter and Drew, J., 1915, **105**, 638; 1916, **107**, 1091; Senter and Tucker, J., 1918, **113**, 140) would be ascribed to a mechanism of the above type.

EXPERIMENTAL.

r-*Phenylmethylcarbinol* was prepared by the slow addition during 3—4 hours of 72 g. of benzaldehyde, dissolved in ether, to a vigorously stirred, ice-cooled solution of magnesium methyl iodide, prepared from 142 g. of methyl iodide. After the mixture had remained at room temperature for ½ hour, the additive compound was decomposed with water and dilute acid. The *r*-phenylmethylcarbinol was purified and isolated in the usual way; b. p. 101—102°/20 mm., yield 63 g.

d-*Phenylmethylcarbinol* was obtained by the resolution of the *r*-carbinol by Pickard and Kenyon's method (J., 1911, **99**, 45) and had $\alpha_{5780}^{15^\circ} + 22{\cdot}19^\circ$ for $l = 0{\cdot}5$; whence $[\alpha]_{5780}^{15^\circ} + 45{\cdot}0^\circ$, compared with Pickard and Kenyon's values $[\alpha]_{D}^{6^\circ} + 42{\cdot}9^\circ$, $[\alpha]_{D}^{27^\circ} + 42{\cdot}85^\circ$.

r-α-*Chloroethylbenzene* was prepared from *r*-phenylmethylcarbinol by means of thionyl chloride (McKenzie and Clough, J., 1913, **103**, 694); the acidity was almost entirely removed by shaking the product with anhydrous potassium carbonate for a short time and then redistilling it; b. p. 81—82°/17 mm. Results of typical analyses of *r*-α-chloroethylbenzene from different preparations of phenylmethylcarbinol are: Cl, (volumetric), 24·75, 24·98, 24·95, 24·96%; (gravimetric), 25·40, 25·24, 25·18, 25·30%. In the volumetric method, the chlorine was determined by heating a solution of α-chloroethylbenzene in aqueous ethyl alcohol, and titrating the liberated acid with standard alkali until the colour change, with phenolphthalein as indicator, was permanent. For the gravimetric analyses, Stepanow's method was used throughout.

The *r*-α-chloroethylbenzene at first used in these experiments was prepared from phenylmethylcarbinol, obtained by the Grignard reaction from 1 mol. of benzaldehyde and 1 mol. of magnesium methyl iodide. The percentage halogen (gravimetric estimation) in different preparations of this material varied from 23·9 to 24·8 (calc., 25·27%). If the displacement of the halogen was carried out in aqueous (20%) ethyl-alcoholic solution at 28·7°, the final titrations corresponded with Cl = 20·1 to 21·0%, these values being considerably lower than those determined by the gravimetric method. This is not due to an equilibrium of the type $CHPhMeX + H_2O \rightleftharpoons CHPhMe{\cdot}OH + HX$, for under the conditions of experiment phenylmethylcarbinol and hydrogen chloride did not react.

As ordinarily prepared, phenylmethylcarbinol is contaminated with impurities (compare Marshall, J., 1914, **105**, 527; 1915, **107**, 509), which doubtless give chloro-derivatives rendering the α-chloroethylbenzene impure. By preparing the phenylmethylcarbinol as above, with 3 mols. of the Grignard reagent to 2 mols. of benzaldehyde, the values for the percentage halogen in the derived chloro-compound, as shown from the preceding analyses, are in much closer agreement when estimated by the two methods, but in all cases the values found by titration are somewhat lower than those obtained by Stepanow's method. The α-chloroethylbenzene used in the following experiments was prepared by this method.

d-α-*Chloroethylbenzene* was prepared from *d*-phenylmethylcarbinol by McKenzie and Clough's method (*loc. cit.*) and purified as above; b. p. 82—83°/18 mm.; $\alpha_{5780}^{21^\circ} + 26{\cdot}08^\circ$, $l = 0{\cdot}5$, $[\alpha]_{5780}^{21^\circ} + 49{\cdot}07^\circ$ (compare McKenzie and Clough, $[\alpha]_D + 50{\cdot}6^\circ$). The percentages of chlorine, determined by the two methods, were (volumetric) 24·77, (gravimetric) 24·86.

β-*Chloroethylbenzene* prepared from β-phenylethyl alcohol and phosphorus pentachloride (Found: Cl, 25·7. Calc.: Cl, 25·3. Barger, J., 1909, **95**, 2194, found Cl, 25·8%) contained a negligible quantity of hydrogen chloride but an appreciable quantity of phosphorus. Thionyl chloride gave a much purer product: β-Phenylethyl alcohol (25 g.) was slowly added to thionyl chloride (40 g.) at room temperature. Vigorous evolution of hydrogen chloride took place, but the mixture did not become appreciably warm. The reaction mixture was kept for about an hour and then distilled; the product, purified with potassium carbonate, had b. p. 83—84°/14 mm. (yield, 25 g.) (Found: Cl, 25·2%).

α-Phenylethyl p-*Nitrobenzoate.*—Phenylmethylcarbinol (1 g.) was dissolved in pyridine (3 g.), and *p*-nitrobenzoyl chloride (1·8 g.) slowly added with cooling. The mixture was kept for 4 hours, treated with excess of dilute sulphuric acid and filtered, and the precipitate was stirred with sodium carbonate solution. The crude ester (2·25 g.) crystallised from aqueous alcohol in pale yellow needles, m.p. 47—48° (Found: equiv. by hydrolysis, 274. $C_{15}H_{13}O_4N$ requires equiv., 271).

Products of the Reaction of r-*α-Chloroethylbenzene with Aqueous Ethyl Alcohol.*—Ethyl alcohol (280 c.c.) and water (70 c.c.), both at 50°, were added to *r*-α-chloroethylbenzene (7·5 g.). The solution was maintained at this temperature for 12 hours, the water then removed by means of potassium carbonate, and the alcoholic solution fractionated, 5·8 g. of liquid, b. p. 71—94°/15 mm., being obtained. A mixture of this with pyridine (17 g.) and *p*-nitrobenzoyl chloride (10 g.) was kept for 4 hours, excess of dilute sulphuric acid was then added, and the pasty product was filtered off, well pressed, and twice washed with some 25 c.c. of ether; 6·2 g. of solid then remained undissolved. The ethereal solution was shaken with the aqueous filtrate, separated, dried, and distilled; α-phenyldiethyl ether (2·55 g.) was then obtained, b. p. 76°/20 mm. (compare Holmberg, *Ber.*, 1912, **45**, 1002, who gives b. p. 71·5—72°/15 mm.) (Found: OEt, 29·5. Calc.: OEt, 30·0%). The residue (6·5 g.) in the distillation flask slowly crystallised. The combined solid products, after treatment with excess of dilute sodium carbonate solution, gave 6·4 g. of crude α-phenylethyl *p*-nitrobenzoate, m. p. 47° after crystallisation from aqueous alcohol.

Similarly, at 28·7°, *r*-α-chloroethylbenzene (5 g.), reacting with ethyl alcohol (280 c.c.) and water (70 c.c.) for 7 days, gave 3·05 g. of product, b. p. 72—90°/13 mm., which, by the above method of separation, yielded 0·85 g. of α-phenyldiethyl ether, b. p. 75°/19 mm. From *r*-α-chloroethylbenzene (5 g.), reacting with ethyl alcohol (280 c.c.) and aqueous 0·967*N*-sodium hydroxide (70 c.c.) at 28·7° for 8 days, 3·45 g. of product, b. p. 72—90°/14 mm., were obtained, from which was separated α-phenyldiethyl ether (1·4 g.), b. p. 71°/15 mm.

In none of these experiments was any evidence obtained of the formation of αα′-diphenyldiethyl ether.

Reaction between r-α-*Chloroethylbenzene and Water.*—(a) A mixture of 300 c.c. of water and 20 g. of *r*-α-chloroethylbenzene [Cl, 24·65% (volumetric), 25·27% (gravimetric)] was gently boiled under reflux for 2 hours; the products were then extracted with ether and dried. On distillation the following fractions were obtained: (1) b. p. 52—53°/23 mm., 1·7 g.; (2) b. p. 111—113°/27 mm., 3·7 g.; (3) b. p. 112—160°/23 mm., 1·9 g.; (4) b. p. 167—168°/23 mm., 6·3 g.

Fraction (1) distilled at ordinary pressure at 145—146° (styrene has b. p. 146°/759 mm.), leaving a colourless gum, doubtless metastyrene. Fraction (2), on treatment with thionyl chloride and subsequent purification as in the preparation of *r*-α-chloroethylbenzene, gave a product (3·45 g.), b. p. 87—88°/24 mm. [Found: Cl, 23·9% (volumetric), 25·26% (gravimetric)]; 0·15 g. distilled at 88—170°/24 mm., and the residue was negligible. Fraction (3), treated in the same way as (2), gave 1·45 g., b. p. 85—86°/22 mm. [Found: Cl, 23·95% (volumetric), 24·81% (gravimetric)], and 0·15 g., b. p. 86—150°/22 mm. Fractions (2) and (3) therefore consisted of phenylmethylcarbinol, with possibly some αα′-diphenyldiethyl ether; the low value for the halogen determination by the volumetric method is probably due to the accumulation in these fractions of the substances present in the original material containing the less reactive halogen. Fraction (4), b. p. 167—168°/23 mm.

(Oddo, *loc. cit.*, records the b. p. of αα'-diphenyldiethyl ether as 240—245°/20 mm., undoubtedly in error for 140—145°/20 mm.; Marshall, *loc. cit.*, gives b. p. 148—150°/15 mm.; Wuyts, *loc. cit.*, gives b. p. 156·5°/17 mm.), a clear, colourless liquid which was free from halogen and underwent no change on prolonged standing with sodium, was αα'-diphenyldiethyl ether (Found: C, 85·2; H, 8·0; *M*, cryoscopic in naphthalene, 209. Calc.: C, 85·0; H, 8·0%; *M*, 226).

(b) This experiment was a repetition of (a), except that the time of boiling was 5 minutes only. The fractions obtained were: (1) b. p. 73—76°/20 mm., 6·4 g.; (2) b. p. 85—120°/30 mm., 0·8 g.; (3) b. p. 173—175°/30 mm., 6·2 g. Estimations of chlorine in the fractions gave (1) 18·4%, (2) 11·8%, (3) nil, corresponding with (1) and (2) being mixtures of α-chloroethylbenzene, styrene, and phenylmethylcarbinol, and (3) being αα'-diphenyldiethyl ether.

(c) The replacement of the halogen was carried out at 50°, a stirred mixture of *r*-α-chloroethylbenzene (25 g.) and water (400 c.c.) being warmed for 12 hours. The product (19 g.) had b. p. 99—105°/20 mm., and therefore was phenylmethylcarbinol alone; some 0·5 g. of liquid remained in the distilling flask.

Reaction between Phenylmethylcarbinol and Water.—*r*-Phenylmethylcarbinol (10 g.) was heated with water (160 c.c.) at 100° for 8 hours. The bulk (7·5 g.) of the product, b. p. 104—106°/24 mm., was unchanged phenylmethylcarbinol; a second fraction (0·8 g.) had b. p. 106—120°/24 mm.

Reaction between Phenylmethylcarbinol and Hydrochloric Acid.—*r*-Phenylmethylcarbinol (20 g.) was heated with hydrochloric acid (320 c.c.; approx. *N*/2) at 100° for 8 hours. The products were (1) styrene, b. p. 54—58°/24 mm., 1·2 g., (2) phenylmethylcarbinol, b. p. 106—109°/24 mm., 2·5 g., (3) αα'-diphenyldiethyl ether, b. p. 163—165°/21 mm., 9·45 g.

Reaction between αα'-Diphenyldiethyl Ether and Hydrochloric Acid.—The ether (15 g.) was heated under the conditions of the preceding experiment. The products were: (1) styrene, b. p. 47—50°/22 mm., 0·35 g., (2) phenylmethylcarbinol, b. p. 118—126°/31 mm., 2·0 g., (3) αα'-diphenyldiethyl ether, b. p. 175—177°/31 mm., 8·95 g.

Kinetic Experiments.

In the following experiments the solvent medium employed throughout was aqueous (20% by volume) ethyl alcohol. The ethyl alcohol used was commercial absolute alcohol, dried by refluxing and distilling over quick-lime. In preparing the solution the substance under investigation was dissolved in ethyl alcohol, the measured volumes of water, hydrochloric acid, or sodium hydroxide added, and the solution made up to volume with ethyl alcohol, all the reactants being at the temperature of experiment. The amounts of carbinol and chloro-compounds used, and also the concentrations of added hydrogen chloride or sodium hydroxide, are expressed in mols. per litre; all titrations are referred to 20 c.c. of the solution against sodium hydroxide ($N/10$) or alcoholic benzoic acid ($N/10$), the actual experimental figures being converted to this basis. In all titration experiments, phenolphthalein was used as indicator. Unless otherwise stated, the values of k are calculated from the formula $k = 2{\cdot}3/t.\ \log_{10}\ \{a/(a-x)\}$ for a unimolecular reaction.

(1) *r*-Phenylmethylcarbinol, 0·0983; hydrogen chloride, 0·0935; temp. 28·5°.

Time (hrs.) ...	0·27	1·1	24·7	48	96	216
Titre	18·60	18·67	18·62	18·71	18·78	18·78

(2) *r*-Phenylmethylcarbinol, 0·1211; hydrogen chloride, 0·1870; temp. 28·5°.

Time (hrs.)	2	72	96	120	144
Titre	37·38	37·39	37·43	37·32	37·69

(3) *r*-α-Chloroethylbenzene, 0·0906; temp. 28·7°.

Time (hrs.).	Titre.	*k*.	Time (hrs.).	Titre.	*k*.
0·1	0·185	—	34·1	15·41	0·0569
3·1	2·93	0·0557	55·35	17·09	0·0541
6·1	5·24	0·0557	144	17·81	—
10·1	7·92	0·0570	192	17·97	—
23·1	13·17	0·0568	240	17·98	—

(4) *r*-α-Chloroethylbenzene, 0·0849; sodium hydroxide, 0·0941; temp. 28·7°.

Time (hrs.).	Titre.	*k*.	Time (hrs.).	Titre.	*k*.
0·1	18·69	—	30·1	4·93	0·0566
3·1	16·13	0·0549	54·1	2·62	0·0571
7·1	13·29	0·0552	122·1	1·86	—
10·6	11·18	0·0561	171·1	1·85	—

(5) *r*-α-Chloroethylbenzene, 0·0890; sodium hydroxide, 0·1882; temp. 28·7°.

Time (hrs.).	Titre.	*k*.	Time (hrs.)	Titre.	*k*.
0·1	37·65	—	54·1	20·66	0·0565
3·1	34·84	0·0569	120·1	19·83	—
7·1	31·91	0·0554	144·1	19·83	—
11·1	29·44	0·0551	168·1	19·82	—
30·1	23·09	0·0565			

The mean values of the velocity coefficients obtained at 50·0°, as in (3), (4) and (5), are summarised below.

Exper.	*r*-α-Chloroethylbenzene.	Sodium hydroxide.	*k*.
(6)	0·0903 mol./l.	—	0·589
(7)	0·0833	0·1025 mol./l.	0·590
(8)	0·0924	0·2050	0·590

(9) *d*-α-Chloroethylbenzene, 0·1071; samples were withdrawn at the times shown, and their rotations determined in a 2 dm.-tube for the yellow mercury line; temp. 28·6°.

Time (hrs.).	$\alpha^{28\cdot6^\circ}_{5780}$.	*k*.	Time (hrs.).	$\alpha^{28\cdot6^\circ}_{5780}$.	*k*.
0·19	+ 1·30°	—	27·00	− 0·09°	0·0598
1·17	+ 1·20	0·0603	30·64	− 0·17	0·0611
3·06	+ 1·02	0·0610	48·94	− 0·33	0·0566
5·07	+ 0·85	0·0612	6 days	− 0·39	—
7·02	+ 0·69	0·0631	10 ,,	− 0·43	—
9·06	+ 0·56	0·0624	27 ,,	− 0·43	—
11·93	+ 0·40	0·0619	159 ,,	− 0·44	—

(10) *d*-α-Chloroethylbenzene, 0·0929; sodium hydroxide, 0·1092. The solution was turbid and was filtered before the measurements were made. The initial rotation ($t = 0\cdot18$ hr.) was $\alpha^{28\cdot6^\circ}_{5780} + 0\cdot85^\circ$, and the final value ($t = 120$ hrs.) was $\alpha^{28\cdot6^\circ}_{5780} - 0\cdot36^\circ$, for $l = 2$. The individual values of *k* varied from 0·0539 to 0·0582, giving a mean of 0·0558.

(11) β-Chloromethylbenzene, 0·0996; temp. 28·9°.

Time (days) ...	0	1	5	11	22	55
Titre	0·11	0·09	0·12	0·22	0·25	0·33

(12) β-Chloroethylbenzene, 0·0975; sodium hydroxide, 0·1858; temp. 28·9°.

Time (days).	Titre.	*k*.	Time (days).	Titre.	*k*.
0·0	37·16	—	4	33·38	0·0016
0·5	36·40	0·0022	8	30·30	0·0016
1·07	35·88	0·0018	19	25·90	0·0015
2·01	35·00	0·0016	26	23·98	0·0015
3·02	34·10	0·0016	52	19·94	0·0016

k is equal to $\dfrac{2\cdot3}{(b-a)t}\log_{10}\dfrac{a(b-x)}{b(a-x)}$, t being measured in days, a, b and x in c.c. of $N/10$-acid.

(13) β-Chloroethylbenzene, 0·0917; sodium hydroxide, 0·0929; temp. 28·9°.

Time (days).	Titre.	*k*.	Time (days).	Titre.	*k*.
0·01	18·48	—	7	14·99	0·0018
0·40	18·35	0·0010	18	11·84	0·0017
1·00	17·79	0·0022	25	10·26	0·0017
2·13	17·34	0·0017	51	6·70	0·0019
3·04	16·95	0·0016			

The formula for a bimolecular reaction where $a = b$, namely, $k = x/ta(a-x)$, was used.

Summary.

(1) The displacement of the halogen in *r*-α-chloroethylbenzene in aqueous ethyl-alcoholic solution alone and also in the presence of sodium hydroxide at 28·7° and at 50·0° yields a mixture of phenyl-

methylcarbinol and α-phenyldiethyl ether; the velocity coefficient obtained in each case is that of a unimolecular reaction, the sodium hydroxide or its ions playing no part in the halogen displacement.

(2) This result is confirmed by a calculation of the velocity coefficients from observations on the change in the rotation of solutions of *d*-α-chloroethylbenzene under comparable conditions.

(3) The displacement of the halogen in β-chloroethylbenzene is in marked contrast to the above; in aqueous ethyl-alcoholic solution the displacement is negligibly slow; in the presence of sodium hydroxide, velocity coefficients of a bimolecular reaction are obtained but the halogen displacement proceeds much more slowly than in the case of α-chloroethylbenzene.

(4) *r*-α-Chloroethylbenzene, on boiling with water, yields mainly αα′-diphenyldiethyl ether, together with styrene and phenylmethylcarbinol. The same products are obtained on boiling phenylmethylcarbinol with *N*/2-hydrochloric acid, and also by submitting αα′-diphenyldiethyl ether to similar treatment.

(5) The experimental evidence under (1), (2), and (4) is in accordance with the reaction proceeding through a phase CPhMe<, in which but two groups are momentarily attached to carbon.

(6) The mechanism under (5) is discussed in connexion with the Walden inversion.

The author wishes to express his thanks to Drs. Senter and Barrow for their valued interest in this research, and also to the Department of Scientific and Industrial Research for a maintenance grant during a part of the time occupied in carrying it out.

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[*Received, November 9th,* 1926.]

LXVII.—*Acid and Salt Effects in Catalysed Reactions. Part VI.* The Early Stages of an Auto-catalysed Reaction. Generalised Form of the Simple Auto-catalytic Catenary.*

By HARRY MEDFORTH DAWSON.

THE investigation of the auto-catalytic reaction between acetone and iodine (Dawson and Powis, J., 1912, **101**, 1503) showed that when the concentration of the acetone is constant, the course of the reaction can be represented very accurately by the simplest possible type of auto-catalytic equation, namely, $dx/dt = kx$, where x, the observed fall in the iodine concentration after time t, affords a measure of the concentration of the hydriodic acid produced; if not too small, this may be taken to represent the hydrogen-ion concentration.

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* Paper V of this series is published in the *Proc. Leeds Phil. Lit. Soc.*, 1926, 1, 108, under the title " Isohydric Solutions and the Velocity of Chemical Change."

With an acetone concentration of 20 c.c. per litre (0·272M), the time required at 25° to reach the stage at which the value of x can be measured by titration with 0·01N-thiosulphate is about 3 days. During this period, the course of the reaction cannot be followed by any direct method,* and one of the objects of this paper is to show how the nature of the changes taking place in the early stages of the reaction may be elucidated by an indirect method.

On extrapolating the straight line obtained by plotting $\log x$ against t, Dawson and Powis obtained a value of x for $t = 0$, which represented the apparent initial hydrogen-ion concentration when it was assumed that the reaction proceeded in its early stages in accordance with the equation found to represent accurately the experimental observations for the later stages. This empirically derived value of x will be referred to in this paper by "x_0." It represents the constant in the integrated form of the differential equation, which may therefore be written $k = 1/t \, . \log_e x/$"x_0".

The experimental data showed that "x_0" is reproducible within narrow limits, but its relatively high value seemed to preclude the possibility that "x_0" could correspond with the true initial hydrogen-ion concentration of the solution. This view was supported by the fact that the addition of small quantities of alkali to the original solution made no difference in the value obtained for "x_0." On the other hand, it was found that the value of "x_0" is reduced by the addition of small quantities of hydrochloric acid and that it becomes equal to zero when the amount of added acid is sufficient to give approximately a $10^{-4}N$-solution.

More recent experiments (Dawson and Carter, J., 1926, 2282) have shown that the hydroxyl ion is a very active catalyst for the acetone–iodine reaction, and it therefore seemed very probable that the participation of hydroxyl ions in the early stages of the auto-catalytic change might be responsible for the above behaviour. It will be shown that this assumption is quite in accordance with the facts and that the initial stage of the auto-catalysed reaction is very different in character from the later stages. The analysis to be described is of particular interest in that it illustrates the possibility of obtaining detailed information relative to the mechanism of a reaction at a stage which is inaccessible to direct experimental observation.

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* Conductivity measurements are not applicable and preliminary attempts to measure the hydrogen potential did not appear to be hopeful.

The Hydrogen-ion Concentration of the Original Solution.

In addition to acetone and iodine, the original solution contained potassium iodide, added in the molecular ratio $KI : I_2 = 2 : 1$ to dissolve the requisite amount of iodine. Since hydrogen ions are produced by ionisation of the solvent and also by hydrolysis of the iodine, it is obviously necessary to inquire under what conditions the hydrogen ions produced by the reaction and measured by x may be taken as a measure of the total hydrogen-ion concentration. It will be shown that this condition is attained when x reaches a value which may be placed at about 2×10^{-6}, and that, from the kinetic standpoint, it is not of any great importance to know the precise value of the hydrogen-ion concentration of the original solution provided that it is not greater than this limiting value.

So far as the hydrogen ions produced by the solvent are concerned, it follows at once from the equation

$$[H^+] . (x + [H^+]) = 10^{-14}$$

that $[H^+]$ may be entirely neglected when $x = 2 \times 10^{-6}$.

In regard to the hydrogen ions produced by hydrolysis of the iodine, consideration must be given to the equilibria

$$I_2 + I^- \rightleftharpoons I_3^-$$

and $$I_2 + H_2O \rightleftharpoons H^+ + I^- + HIO.$$

The constant characteristic of the first equilibrium $K_1 = [I_2] . [I^-]/[I_3^-]$ is equal to $1{\cdot}38 \times 10^{-3}$ (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19). For the second, the value of $K_2 = [H^+] . [I^-] . [HIO]/[I_2]$, according to measurements of the electrical conductivity of a saturated solution of iodine in pure water, is equal to $0{\cdot}6 \times 10^{-12}$ (Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 932). The value of this constant is not nearly so trustworthy as K_1, but its accuracy is probably quite sufficient for the present purpose.

In the auto-catalytic experiments, the concentrations of the iodine and potassium iodide were for the most part 0·004 and 0·008 mol. per litre, respectively. Introducing these values into the equation for K_1, it may be shown that the ratio $[I_2]/[I^-]$ is approximately equal to 0·18. This ratio remains constant in the initial stage of the auto-catalytic change, and by reference to the equation for K_2, since $[H^+] = [HIO]$, it follows that the initial hydrogen-ion concentration due to iodine hydrolysis is given by $[H^+]_0 = \sqrt{K_2 . [I_2]/[I^-]} = 3{\cdot}3 \times 10^{-7}$. When x mols. of hydriodic acid have been produced by the acetone reaction, the concentration

$[H^+]$ of the hydrogen ions resulting from iodine hydrolysis is given by

$$[H^+] . (x + [H^+]) = (3{\cdot}3 \times 10^{-7})^2,$$

from which, if $x = 2 \times 10^{-6}$, the value obtained for $[H^+]$ is $0{\cdot}5 \times 10^{-7}$. In other words, the hydrogen ions formed by iodine hydrolysis represent only 2·5% of the total when $x = 2 \times 10^{-6}$ and may therefore without serious error be left out of account.

The foregoing analysis is necessarily antecedent to the dynamic considerations which follow. The practical outcome of it is that the total hydrogen-ion concentration throughout the initial period is determined by the concentration (x) of the auto-catalytically produced hydrogen ion. The interval for which this is not true is negligibly small.

Dynamics of the Auto-catalysed Reaction.

In accordance with the assumption that the course of the autocatalytic change is determined by the joint action of the hydrogen and hydroxyl ions, we have

$$v = v_h + v_{OH} = k_h[H^+] + k_{OH}[OH^-] \quad . \quad . \quad . \quad (1)$$

In conformity with the preceding analysis and the equation $[H^+] . [OH^-] = K_w$, equation (1) may be written

$$v = dx/dt = k_h x + k_{OH} . K_w/x \quad . \quad . \quad . \quad . \quad (2)$$

The speed of the reaction at any particular moment cannot of course be directly measured, but by integration of (2) an equation is obtained which expresses the time required for the reaction to proceed to any point represented by x. This takes the form

$$t = 1/2k_h . \log_e (k_h x^2 + k_{OH} . K_w) + \text{const.} \quad . \quad . \quad (3)$$

or, if $x = x_0$ (the true initial hydrogen-ion concentration) when $t = 0$,

$$t = 1/2k_h . \log_e (k_h x^2 + k_{OH} . K_w)/(k_h x_0^2 + k_{OH} . K_w) \quad . \quad (4)$$

By differentiation of (2) we obtain

$$dv/dx = k_h - k_{OH} . K_w/x^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

from which it is apparent that the velocity passes through a minimum when

$$x = x_i = \sqrt{k_{OH} . K_w/k_h} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This minimum velocity is given by

$$v_i = 2\sqrt{k_{OH} . K_w . k_h} = 2k_h . x_i \quad . \quad . \quad . \quad . \quad (7)$$

Substituting in (4) the value of $k_{OH} . K_w$ given by (6), we obtain

$$t = 1/2k_h . \log_e (x^2 + x_i^2)/(x_0^2 + x_i^2) \quad . \quad \quad . \quad (8)$$

The time required for the auto-catalytic change to proceed to any stage measured by a fall in iodine concentration equal to x may thus be calculated from (4) or (8).

If x is large and x_0 small relatively to x_i, these equations may be written

$$t = 1/2k_h \,.\, \log_e k_h x^2/k_{\text{OH}} \,.\, K_w \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4\text{A})$$

and

$$t = 1/2k_h \,.\, \log_e x^2/x_i^2 = 1/k_h \,.\, \log_e x/x_i \quad . \quad . \qquad (8\text{A})$$

respectively. If x_i in equation (8A) is replaced by "x_0," it becomes identical with the empirical equation used by Dawson and Powis. It is thus possible to give a simple interpretation to the empirical quantity "x_0" which was introduced as a measure of the apparent initial acidity in conformity with the simple hydrogen-ion theory of catalysis. It is indeed evident that "x_0" is a measure of the hydrogen-ion concentration at the point of minimum velocity. We have therefore

$$\text{“}x_0\text{”} = x_i = \sqrt{k_{\text{OH}} \,.\, K_w/k_h} \quad . \quad . \quad . \quad . \qquad (9)$$

and since k_h, K_w, and "x_0" are known, this relation may be used for the determination of k_{OH}. For "x_0" the mean value of four experiments recorded by Dawson and Powis is $2{\cdot}07 \times 10^{-5}$, and since $k_h = 4{\cdot}68 \times 10^{-4}$ * and $K_w = 10^{-14}$, we obtain

$$k_{\text{OH}} = 19{\cdot}9 \text{ (say 20).}$$

According to this result, the activity of the hydroxyl ion is about 43,000 times that of the hydrogen ion.

An approximate evaluation of k_{OH} was attempted by Dawson and Carter from observations on the catalytic activity of mixtures of acetic acid and sodium acetate belonging to the series $(0{\cdot}2 - x)CH_3{\cdot}CO_2H + xCH_3CO_2Na$, from which $k_{\text{OH}} = 10$. There can be no doubt that very much greater weight must be attached to the value given by the auto-catalytic experiments.

In reference to equations (8) and (8A) it may be noted that the experimental constancy of "x_0" justifies the conclusion that the true initial hydrogen-ion concentration (x_0) of the acetone–iodine–iodide solution is so small compared with that corresponding with minimum velocity (x_i) that x_0^2 may be neglected in comparison with x_i^2.

From equation (8) the time required to reach the value $x = 2 \times 10^{-6}$ (see pp. 460, 461) is found to be $t = 9{\cdot}7$ minutes. This is very small compared with the time which elapses before the reaction reaches the measurable stage (not less than 3 days), and it follows

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* The coefficient given by Dawson and Powis is 0·1035 (time in hours, acetone concentration = $1M$); when time is expressed in minutes, and the coefficient is referred to 20 c.c. of acetone per litre, it has the value $4{\cdot}68 \times 10^{-4}$.

that the commencement of the reaction could be identified without appreciable error with the time at which the total hydrogen-ion concentration begins to be determined by the auto-catalytically produced hydrogen ion.

It is of interest to note that the total time of reaction given by (8) may be divided into two periods, the first (t_1) representing the time required for the attainment of minimum velocity, whilst the second (t_2) represents the period in which the velocity of the reaction is continually increasing. The values of t_1 and t_2 are given by

$$t_1 = 1/2k_h \, . \log_e (x_i^2 + x_i^2)/x_i^2 = 1/2k_h \, . \log_e 2 \quad . \quad . \quad (10)$$

$$t_2 = 1/2k_h \, . \log_e (x^2 + x_i^2)/2x_i^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10\text{A})$$

Substituting $k_h = 4{\cdot}68 \times 10^{-4}$, equation (10) shows that the maximum time required for the attainment of minimum velocity is 12 hrs. 20 minutes. If the p_H value of the original solution is greater than 6, the actual time will differ from the maximum time by less than 5 minutes, and the actual and maximum times may therefore be regarded as identical.

We may now proceed to make a comparison of the time observed for the reaction to proceed to a given point in the measurable stage with that calculated from the general equation (8). Provided that the point in question lies within the measured region, its actual value is not of any great importance. It may be conveniently taken as the point corresponding with $x = 10^{-3}$ ($p_H = 3$). When a 25 c.c. sample of the solution is titrated with 0·01*N*-thiosulphate, this corresponds with a fall of 5·0 c.c. in the amount of thiosulphate required, a quantity which can be measured without sensible error. The observed times are those derived from the straight-line plots of log x against t. The relevant data are given in Table I. In all the experiments, with one exception, the original solution contained 20 c.c. of acetone, 0·004 mols. of iodine and 0·008 mols. of potassium iodide per litre. In Expt. 3, the concentrations of the iodine and iodide were respectively 0·005 and 0·01. When alkali or acid was added, this is shown in column 2.

TABLE I.

Expt. No.	Substances added to the iodine–iodide solution.	$t_{obs.}$ (hrs.).	$t_{cal.}$ (hrs.).
1	None.	133	138
2	None.	135·5	138
3	None.	141	138
4	4×10^{-5} *N*-NaOH	138	138
5	2×10^{-5} *N*-HCl	121	126
6	4×10^{-5} *N*-HCl	107	112
7	8×10^{-5} *N*-HCl	88	89

The agreement between the observed and the calculated time intervals is such as to justify the conclusion that the course of the auto-catalytic change is in accordance with the views which have been put forward.

In order to facilitate the visualisation of the early stages of the reaction, the appended diagram (upper curve) shows the variation of $\log x$ with t. In the measurable stage, the relation between these is linear, but in accordance with the equation

$$d \log x/dt = k_h + k_{OH} \cdot K_w/x^2 \quad . \quad . \quad . \quad . \quad (11)$$

[an alternative form of equation (2)] the slope of the initial portion of the curve increases continuously as x diminishes. The lower curve in the diagram shows the dependence of the reaction velocity on the time. In drawing this curve, corresponding values of x and t were derived from equation (8) on the assumption that x_0 is negligibly small, and the required velocities were then calculated from equation (2). The relevant numbers are shown in Table II.

FIG. 1.

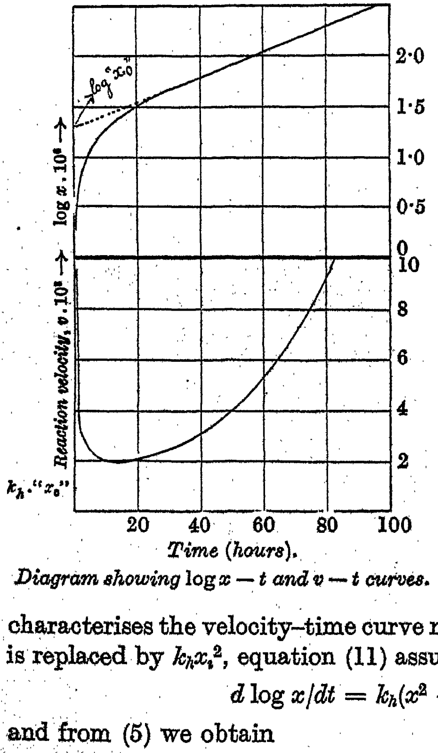

Diagram showing $\log x - t$ *and* $v - t$ *curves.*

In the region of actual measurement, the velocity–time curve is exponential and corresponds with the equation $v = k_h \cdot x_i \cdot e^{k_h t}$, which represents the integrated form of $dx/dt = k_h x$ when the value of x for $t = 0$ is made equal to $x_i =$ "x_0."

A further relation which characterises the velocity–time curve may be noted. When $k_{OH} \cdot K_w$ is replaced by $k_h x_i^2$, equation (11) assumes the form

$$d \log x/dt = k_h(x^2 + x_i^2)/x^2 \quad . \quad . \quad . \quad . \quad (12)$$

and from (5) we obtain

$$dv/d \log x = k_h(x^2 - x_i^2)/x \quad . \quad . \quad . \quad . \quad (13)$$

Combining these equations, there results

$$dv/dt = k_h^2(x^4 - x_i^4)/x^3 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which, for relatively large values of x, takes the form

$$dv/dt = k_h^2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which may, of course, be obtained directly from $v = k_h \cdot$ "x_0" $\cdot e^{k_h t}$.

TABLE II.

$x \,.\, 10_6$.	p_H.	t (mins.).	$v \,.\, 10^8$.	$x \,.\, 10^6$.	p_H.	t (mins.).	$v \,.\, 10^8$.
2	5·70	9·7	10·1	50	4·30	2055	2·74
4	5·40	39·1	5·19	100	4·00	3410	4·88
6	5·22	86·6	3·62	200	3·70	4860	9·46
8	5·10	149	2·88	500	3·30	6820	23·5
10	5·00	225	2·47	1000	3·00	8290	46·8
20·7	4·68	740	1·94				

The asymmetry of the velocity–time curve, as shown by the diagram, is at once apparent from equation (14).

Generalised Form of the Auto-catalytic Catenary.

In previous papers (Dawson and Dean, J., 1926, 2872; Dawson and Hoskins, J., 1926, 3166), it was shown that the catalytic effects resulting from the joint action of the positive and negative ions produced by the ionisation of an acid of constant concentration can be represented by a catenary curve when the reaction velocity is plotted against p_H. The curve connecting the velocity of the autocatalytic change discussed in this paper with $\log x$ (or p_H) is of exactly the same type [compare equation (5)]. In reference to the auto-catalytic catenary, it is to be noted, however, that this represents the *actual* course of the chemical change. The movement of an index point along the catenary corresponds *de facto* with the continuously successive stages of the auto-catalysed reaction.

Following the procedure described in the derivation of the general catalytic catenary (Dawson, this vol., p. 215), and expressing the auto-catalytic reaction velocity in terms of the minimum velocity ($r = v/v_i$), and the hydrogen-ion concentration in terms of its value at the point of minimum velocity ($n = x/x_i$), it may be shown that the reduced velocity r at any stage of the reaction is given by

$$r = \tfrac{1}{2}(n + 1/n) = \tfrac{1}{2}(e^h + e^{-h}) = \cosh h \quad . \quad . \quad (16)$$

where h is the natural logarithm of the reduced hydrogen-ion concentration, n.

Since this equation contains no specific constants, it represents a generalised form of auto-catalytic catenary which should be applicable to all auto-catalysed reactions of the type under discussion. It should therefore be independent of the nature of the particular substances taking part in the change, of the temperature, and of the solvent.

Summary.

It has been shown that the phenomena associated with the autocatalytic reaction of acetone with iodine in aqueous solution can be interpreted in terms of the joint catalytic activity of the hydrogen and hydroxyl ions.

Equations have been derived which show that the reaction velocity falls to a minimum and then increases.

The time calculated for the reaction to proceed to any given point is in close agreement with experiment.

The constant which in terms of the simple hydrogen-ion theory appears to measure the initial hydrogen-ion concentration is found to represent the actual hydrogen-ion concentration at the point of minimum velocity.

The value of this constant affords a means of determining the catalytic coefficient of the hydroxyl ion.

It is further shown that the auto-catalytic catenary obtained by plotting v against p_H can be put into a general form by expressing the velocity and hydrogen-ion concentration in terms of those values which characterise the point of minimum velocity. The actual course of the auto-catalytic change is then given by $r = \cosh h$, where r is the reduced velocity and h is the natural logarithm of the reduced hydrogen-ion concentration.

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[*Received, January 4th,* 1927.]

LXVIII.—*The Partition of Hydrogen Chloride between Water and Benzene.*

By RICHARD WINTON KNIGHT and CYRIL NORMAN HINSHELWOOD.

THE well-known method of determining the state of substances in solution by partition experiments can be utilised to throw light upon the state of strong electrolytes dissolved in water.

Debye and Hückel have shown that when the apparent degree of dissociation of such an electrolyte is corrected for the effect of the inter-ionic forces on the conductivity and on the osmotic pressure, the result is nearly unity for solutions of moderate concentration. This is referred to as complete dissociation. The result does not prove the absolute non-existence of un-ionised molecules, but simply shows that their concentration, if they do exist, is very much smaller than was supposed before the proper corrections were introduced.

There is, on the other hand, positive evidence for the existence of un-ionised molecules, if only in extremely small concentration, wherever there is a definite partition between water and some non-polar solvent. Little work has been done on the partition of strong electrolytes, because it is difficult to find one having a sufficiently great solubility in a suitable non-polar solvent, a fact which itself indicates the reluctance with which un-ionised molecules are formed. Among the most important papers bearing on the subject are those of Hill (*J. Amer. Chem. Soc.*, 1921, **43**, 254), on the partition of silver perchlorate between water and benzene, Rothmund and Drucker (*Z. physikal. Chem.*, 1903, **46**, 827), on picric acid and the same two solvents, and Cavanagh (*Proc. Roy. Soc.*, 1924, [*A*], **106**, 243), on the partition of lithium chloride between water and amyl alcohol.

At sufficiently high concentrations aqueous solutions of hydrogen chloride have a considerable partial pressure of gaseous hydrogen chloride, showing that un-ionised molecules must exist in solution. It seemed likely that further information would be obtained by studying the partition of hydrogen chloride between water and benzene up to concentrations as high as possible. The work now described does not aim at establishing standard values for the various solubilities, but only at showing the general nature of the partition relationships. Nevertheless, it seems to show quite clearly that there is a definite equilibrium in water between ionised and un-ionised hydrogen chloride. Up to a concentration of about 10*N* there is only a very small proportion of un-ionised molecules, in accordance with the results of Debye and Hückel, a fact which can also be seen from the vapour-pressure results. Above about 15*N*, however, the proportion of un-ionised molecules becomes very considerable, and in the region 15—20*N* there is a roughly constant partition coefficient, indicating that the state of the greater part of the hydrogen chloride in the water is the same as its state in the benzene.

No information could be found about the solubility of hydrogen chloride in benzene. This was therefore determined. The solubility in water is given in most standard works, but all data appear to rest upon the original determination of Roscoe and Dittmar (J., 1860, **12**, 128). The value was therefore re-determined at 20° by a different method.

The benzene was prepared from the purest " Analytical Reagent." It was first extracted with pure concentrated sulphuric acid, after which it showed no trace of the indophenin reaction. It was then fractionated through a 6-foot column and collected in large flasks provided with syphons, all corks used being covered with pure tinfoil. It was subsequently twice purified by freezing. The final m. p.'s of four portions were 5·48°, 5·48°, 5·47°, and 5·47° (correct to 0·02°). (Sidgwick, J., 1920, **117**, 1340, gives 5·49° for pure benzene.)

The hydrogen chloride was made by the action of pure sulphuric acid, free from nitrate (diphenylamine reaction), on fused ammonium chloride, free from carbonate and nitrate. The gas was passed through two towers tightly packed with glass wool and was frequently tested for sulphuric acid spray; none was detected.

Pipettes and burettes were standardised by weight.

For experiments in which the concentration was so low that there was no fuming, 400-c.c. glass bottles with ground stoppers and special caps were used. About 80 c.c. each of benzene and distilled water were placed in a bottle and hydrogen chloride was bubbled in for the requisite time. The bottle was then placed in a rocker in a thermostat at 20·00° for 6 hours, the contents were allowed to settle during a further 3 hours, and the two layers were removed by syphons. The aqueous layer was titrated with baryta. The hydrogen chloride in the benzene layer was determined by extracting 10 c.c. with 50 c.c. of boiled-out water, and estimating the hydrogen-ion concentration of the extract by means of " universal indicator " and suitable standards. The results are given in Table III. They show the order of magnitude, only, but it is evident that up to a concentration in the water of about 100 g./litre the amount passing into the benzene is very small indeed. Some of that even will be due to the water dissolved in the benzene, so that the values at these very low concentrations are not suitable for such purposes as the calculation of " activities."

FIG. 1A.

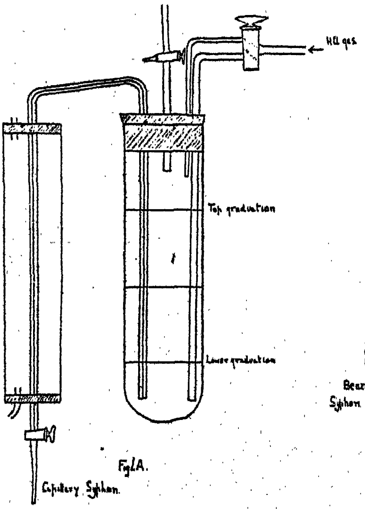
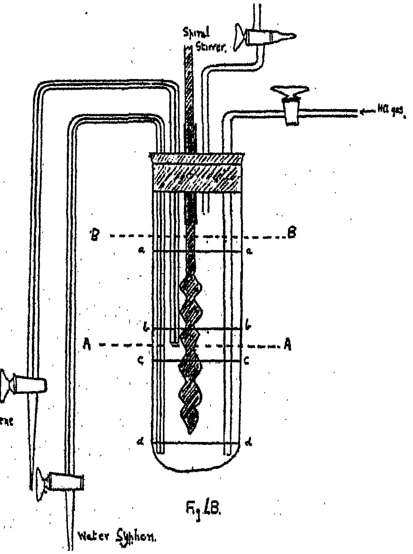


FIG. 1B.



The next determinations made were the solubilities of hydrogen chloride in (1) dry benzene; (2) water; (3) benzene saturated with water before saturation with hydrogen chloride; and (4) benzene saturated with water and hydrogen chloride simultaneously.

For measuring the solubility in dry benzene, the saturator used is shown in Fig. 1A. It was graduated, with all tubes in position, to deliver two amounts of 50 c.c. by means of a capillary syphon. The calibrations were found to be correct at 20°, to within about 0·01 c.c., by weighing water. Two inlet tubes for the hydrogen chloride were provided, one reaching below the lower graduation and the other just entering the vessel so that a stream of gas could be passed over the surface of the liquid when necessary. The gas escaped at atmospheric pressure. The syphon by which the liquid was removed was surrounded by a jacket kept filled with water at 20°. The saturator was placed in a thermostat and filled to just above the top graduation with benzene; and dry hydrogen chloride, after passing through a glass coil immersed in the thermostat, was bubbled through for many hours. The benzene was then run out as far as the top graduation, a stream of gas being passed over the surface all the time. The syphon was thus filled with saturated benzene. 50 C.c. were then run slowly into standard alkali, the jet of the syphon being kept below the surface of the liquid. The excess of alkali was titrated, phenolphthalein being used as indicator, since methyl-red is too soluble in benzene.

The results are summarised in Table I for 20·00°.

TABLE I.

Expt.	Duration of saturation (hrs.).	Pressure (mm.).	Solubility (g./litre of solution).
1	60	760·4	16·80
2	60	761·0	16·76
3	60	760·4	16·82
4	60	762·0	16·74
5	60	761·4	16·79
6	72	760·8	16·81
7	90	759·9	16·80
		Mean at 760 mm.	16·80

For determining the solubility in water at 20·00° (Table II), a smaller saturator delivering 10 c.c. was used, and 24 hours were sufficient for saturation.

TABLE II.

Expt.	Duration of saturation (hrs.).	Pressure (mm.).	Solubility (g./litre of solution).
1	24	760·0	718·8
2	24	766·1	717·9
3	24	762·4	718·8
4	24	762·3	718·5
5	36	760·1	718·8
		Mean at 760 mm.	718·8

The solubility in benzene previously saturated with water was found to be somewhat higher than in dry benzene: at 20·00° and atmospheric pressure, the results obtained were 18·28, 18·28, 18·32, 18·32, and 18·32 g. per litre.

This value cannot be used in conjunction with the solubility in water to determine the partition ratio at the saturation point, since when the wet benzene becomes saturated with hydrogen chloride it may take up a further amount of water and consequently still more hydrogen chloride. Accordingly, water was introduced into the saturator so that it covered the end of the long hydrogen chloride inlet tube but did not reach to the bottom of the syphon. The results for the solubility under these conditions were 18·47, 18·50, 18·50, and 18·50 g. HCl per litre.

We thus have at 20·0° and 760 mm. :

Solubility of hydrogen chloride in water	718·8	g. per litre.
Solubility of hydrogen chloride in dry benzene	16·80	,, ,,
Solubility of hydrogen chloride in benzene previously saturated with water	18·31	,, ,,
Solubility of hydrogen chloride in benzene simultaneously saturated with water and hydrogen chloride	18·50	,, ,,

For partition experiments at high concentrations the apparatus in Fig. 1 B was used. It consisted of a glass tube with four etched graduations *aa*, *bb*, *cc*, and *dd*. The volume contained between *aa* and *bb* and between *cc* and *dd* was 50 c.c. The apparatus was calibrated with the tubes in position and with the stirrer lowered to the bottom of the vessel. Two syphons were provided; that to take off the top layer extended for 1 cm. below *bb*, while the other, to take off the bottom layer, extended for 1 cm. below *dd*. Both were made of capillary tubing and were lagged with cotton wool. The apparatus was placed in the thermostat, filled to AA with pure water and then to BB with benzene. Hydrogen chloride was passed in for periods varying from 1 to 48 hours, according to the concentration required. The spiral stirrer was very efficient, breaking up the benzene into tiny globules and distributing these throughout the aqueous layer. After the gas had been allowed to pass for the requisite time, it was turned off, and the stirring was continued for another 2 hours. The stirrer was then disconnected and lowered to the bottom, since the apparatus had been calibrated with it in this position. The two layers were allowed to separate. The benzene was then run down to the graduation *aa*, thereby filling the syphon with solution of the same concentration as that in the bulk of the apparatus. This procedure also served to remove the top layer, which might have gained or lost a little hydrogen chloride during the settling. 50 C.c. of the benzene layer were then run out into standard alkali and titrated. The whole procedure was immediately repeated with the aqueous layer.

The results (Table III) are expressed as g./litre, C_w and C_B representing the concentrations in the water and benzene phases, respectively.

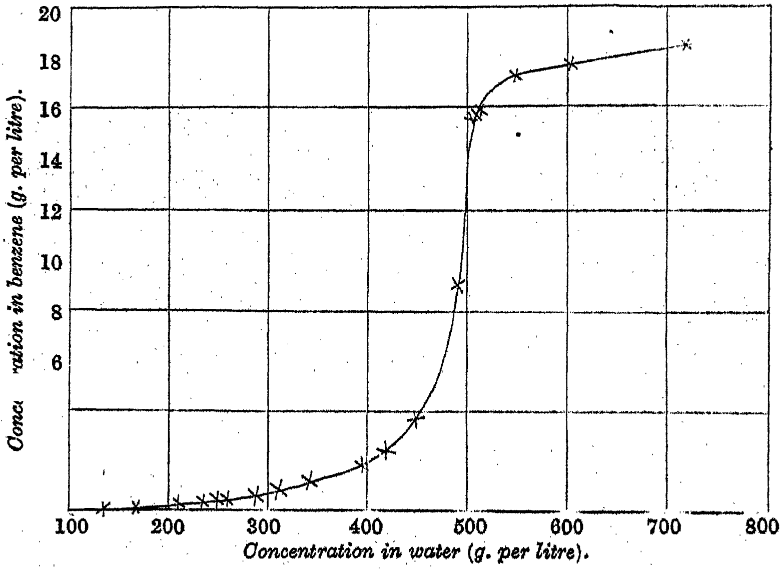
TABLE III.

Partition of Hydrogen Chloride between Water and Benzene at 20·0°.

C_w.	C_B.	C_w/C_B.	C_w.	C_B.	C_w/C_B.	C_w.	C_B.	C_w/C_B.
718·8	18·50	38·85	397·3	1·85	196·0	165·9	0·100	1660
604·0	17·7	34·1	379·8	1·818	208·9	134·6	0·059*	$2{\cdot}3\times10^3$
549·3	17·4	31·6	343·3	1·264	272	94·8	0·028	$3{\cdot}4\times10^3$
513·3	15·99	32·1	312·0	0·929	336	71·9	$1{\cdot}5\times10^{-2}$	$4{\cdot}7\times10^3$
509·0	15·71	32·4	289·3	0·706	410	43·3	$3{\cdot}6\times10^{-3}$	$1{\cdot}2\times10^4$
504·6	15·62	34·2	259·0	0·532	504	34·5	$1{\cdot}8\times10^{-3}$	2×10^4
492·5	8·96	55·0	249·0	0·449	554	19·5	2×10^{-4}	10^5
448·5	3·72	120·7	236·1	0·382	619	12·3	10^{-4}	$1{\cdot}3\times10^5$
420·2	2·47	170·0	212·0	0·252	840			

* The figures for C_B at and below this point are obtained from colorimetric estimations of hydrogen-ion concentration only; the others are based on volumetric titrations.

FIG. 2.



Distribution of hydrogen chloride between benzene and water at 20°.

It is evident from Fig. 2 that, at concentrations between 400 and 550 g./litre in the aqueous layer, there is a rapid passage from the polar to the non-polar form. When this is complete, there is a more or less constant partition ratio as shown by the table. If we regard the concentration in benzene as a measure of the amount of un-ionised hydrogen chloride in the water, then the shape of the curve in Fig. 2 is quite characteristic of an equilibrium between the ionised and un-ionised forms, the change from one to the other being about half complete at a concentration of about 490 g./litre.

According to uncorrected conductivity and osmotic data, this half-way point would come at much lower concentrations, where the Debye–Hückel theory shows ionisation to be still practically complete. The partition method reveals more nearly the true state of affairs.

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LXIX.—*Benzyl δ-Chlorobutyl Ether: A New Unsymmetrical Derivative of Tetramethylene Glycol.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

THE preparation of tetramethylene dibromide is no longer a very difficult matter (v. Braun and Lemke, *Ber.*, 1922, **55**, 3526; Marvel and Tanenbaum, *J. Amer. Chem. Soc.*, 1922, **44**, 2645), but unsymmetrical δ-substituted *n*-butyl halides, which have a special importance as synthetic reagents, have been obtained in only two instances and in poor yield. δ-Amyloxy-*n*-butyl bromide was isolated by Hamonet (*Bull. Soc. chim.*, 1905, **33**, 513) and used in a synthesis of pentamethylene dibromide, whilst δ-phenoxybutyl bromide appeared as a by-product in the conversion of δ-phenoxybutyl alcohol into tetramethylene dibromide described by Marvel and Tanenbaum (*loc. cit.*).

Being in need of an unsymmetrical αδ-disubstituted butane of this type, we decided to prepare δ-benzyloxybutyl chloride (benzyl δ-chlorobutyl ether), since the benzyl group has considerable advantages over both the phenyl and the amyl group in respect of the ease with which it is removed and of the fact that a free hydroxyl group is left in the process. This was a point so vital for the purpose we had in view (see succeeding paper) as to render comparatively unimportant our lower yield of δ-benzyloxybutyl alcohol as compared with that of phenoxybutyl alcohol obtained by Marvel and Tanenbaum.

Benzyl β-chloroethyl ether (Bennett, J., 1925, **127**, 1277) showed no tendency to combine with magnesium, an observation which was consistent with the statement by Hamonet (Wurtz, "Dictionnaire de Chimie," 2, 751) that ethers of the type $RO{\cdot}CH_2{\cdot}CH_2X$ (where X is a halogen) do not yield Grignard reagents. Benzyl iodoethyl ether, however, combined readily with magnesium. The action of the resulting organo-magnesium compound on β-chloroethyl *p*-toluenesulphonate (compare Gilman and Beaber, *J. Amer. Chem. Soc.*, 1923, **45**, 839), on ethylene oxide and on ethylene chlorohydrin (compare Grignard, *Compt. rend.*, 1903, **136**, 1260; 1905, **141**, 44; Meisenheimer, *Annalen*, 1925, **442**, 180) was studied, but in no case did we isolate enough of the desired product for its identification with certainty, and experiments in this direction were abandoned after we had confirmed the original statements of Grignard.

The method of preparation finally adopted involved the reduction of ethyl γ-benzyloxybutyrate to the δ-benzyloxybutyl alcohol. The required ester was obtained in two ways: (*a*) from ethylene glycol through benzyl chloroethyl ether by the malonic ester method, and (*b*) from trimethylene glycol through its monobenzyl ether, benzyl chloropropyl ether and the corresponding nitrile, $CH_2Ph\cdot O\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN$. The practical success of each of these methods depends on the use of thionyl chloride in presence of dimethylaniline to replace the hydroxyl group by chlorine (Darzens, *Compt. rend.*, 1911, **152**, 1314). On the other hand, the corresponding reaction with thionyl bromide has proved less useful, for benzyl γ-hydroxypropyl ether was only partly converted by it into benzyl bromopropyl ether. As the yield was poor and the product impure, a valuable substance for use as an organo-magnesium compound remains inaccessible. With a cheap supply of trimethylene glycol available, the method (*b*) is the more economical, but the yields by the method (*a*) were good.

EXPERIMENTAL.

Benzyl γ-Hydroxypropyl Ether.—The dissolution of sodium metal in hot trimethylene glycol involves considerable charring and the reaction may become uncontrollable if the metal is allowed to melt (compare Noyes, *Amer. Chem. J.*, 1897, **19**, 766). The method recently used (J., 1925, **127**, 1279) with ethylene glycol is inadvisable, since trimethylene glycol forms a stable compound with sodium ethoxide (Parone, *Boll. Chim. Farm.*, 1905, **44**, 481). The required sodium compound was conveniently obtained as follows: To trimethylene glycol (240 g.), covered with dry xylene (200 c.c.) and heated to 130°, sodium (25 g.) was cautiously added in small pieces. The reaction was easily controlled and soon complete. To the mixture, cooled to 120°, benzyl chloride (150 g.) was added in small portions, and the reaction completed by boiling the whole for 15 minutes. After addition of benzene to increase the precipitation of the sodium chloride, the solution was filtered, washed with water and dried, the solvents were evaporated, and the product was distilled under diminished pressure. The residue of high b. p. containing the dibenzyl ether of the glycol was neglected. *Benzyl γ-hydroxypropyl ether* is an almost colourless oil, b. p. 155°/23 mm., 172°/43 mm., $d_{4^{\circ}}^{20^{\circ}}$ (vac.) 1·0474, $n_{\alpha}^{20^{\circ}}$ 1·5128, whence $[R_L]_{\alpha}$ 47·77 (calc., 47·64). It is not miscible with water, but is soluble in alcohol and ether (Found: C, 71·8; H, 8·5. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·5%). The yield of this monobenzyl ether (128 g.; 70%) was reduced when the temperature of the reaction was higher than 120°. This is to be expected if, as is the case with ethylene glycol (Forcrand, *Compt. rend.*, 1891, **113**, 1048), the heat evolved in the replacement of the second atom of hydrogen by sodium is less than that for the first, since this will cause a redistribution of the equilibrium in the mixture in favour of the disodium compound as the temperature rises. Attempts to prepare a *p*-nitrobenzoate and a phenylurethane derivative of the substance yielded no crystalline products other than *p*-nitrobenzoic acid and diphenylcarbamide.

Benzyl γ-Chloropropyl Ether.—Thionyl chloride (120 g.) was added drop by drop to a mixture of benzyl hydroxypropyl ether (160 g.) and dimethylaniline (130 g.) below 60°. After ½ hour, the mixture was poured into dilute hydrochloric acid in excess, and the heavy oil which separated removed with chloroform. The extract was washed with dilute acid to remove dimethylaniline, then with water, and dried over sodium sulphate, the solvent evaporated, and the oil distilled. *Benzyl γ-chloropropyl ether* was at once obtained (153 g.; 83% yield) as a colourless oil, b. p. 129°/16 mm., $d_{4^{\circ}}^{20^{\circ}}$ (vac.) 1·0706, $n_{\alpha}^{20^{\circ}}$ 1·5102, whence $[R_L]_{\alpha}$ 50·40 (calc., 50·96) (Found: Cl, 19·4. $C_{10}H_{13}OCl$ requires Cl, 19·2%).

γ-Benzyloxybutyronitrile, $CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$.—A solution of benzyl chloropropyl ether (200 g.) and sodium cyanide (85 g.) in water (100 c.c.) and industrial spirit (125 c.c.) was boiled under reflux for 48—60 hours, any alcohol evaporating being replaced from time to time. Benzene was added when the mixture had cooled, and the sodium chloride was then filtered off and the upper layer of benzene was removed, dried over sodium sulphate and distilled in a Widmer vacuum fractionating flask (*Helv. Chim. Acta*, 1924, **7**, 59), a complete separation of the nitrile from any unchanged chloro-compound being thus readily secured; a second distillation gave the analytically pure *γ-benzyloxybutyronitrile*, a colourless oil of faint odour, b. p. 157°/12 mm., 166°/16 mm., $d_{4^{\circ}}^{20^{\circ}}$ (vac.) 1·026, $n_{\alpha}^{20^{\circ}}$ 1·5005, whence $[R_L]_{\alpha}$ 50·27 (calc., 50·61) (Found: C, 75·2; H, 7·7. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5%). The yield of nitrile was 100—110 g. (57%) and 25—40 g. of chloropropyl ether were recovered (16%).

Ethyl γ-Benzyloxybutyrate, $C_7H_7·O·CH_2·CH_2·CH_2·CO_2Et$.—The nitrile (82 g.) was boiled under reflux with absolute ethyl alcohol (95 g.) and concentrated sulphuric acid (45 g.) for 8 hours, half the alcohol removed by distillation, and the residue poured into water. The precipitated oil was separated by means of ether, the extract washed with sodium carbonate solution, dried, and distilled. *Ethyl benzyloxybutyrate* (63—69 g.; 65% yield) was thus obtained as a straw-coloured oil, b. p. 160°/14 mm., $d_{4^\circ}^{20^\circ}$ (vac.) 1·036, $n_{\alpha}^{20^\circ}$ 1·4930, whence $[R_L]_{\alpha}$ 62·10 (calc., 61·56) (Found: C, 70·5; H, 8·2. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·2%).

Alternative Synthesis of Ethyl Benzyloxybutyrate.—A mixture of ethyl malonate (24 g.), benzyl β-chloroethyl ether (25·6 g.), and sodium ethoxide (from 3·5 g. of sodium) in absolute ethyl alcohol (50 c.c.) was heated in a soda-water bottle at 100° for 6 hours. The alcohol and any unchanged material were removed in a current of steam, the residual oil was separated in ether, and the extract was washed, dried and distilled; *ethyl β-benzyloxyethylmalonate*, $C_7H_7·O·CH_2·CH_2·CH(CO_2Et)_2$ (17 g.), was then obtained as a colourless liquid of b. p. 213°/22 mm., $d_{4^\circ}^{20^\circ}$ (vac.) 1·0795, $n_{\alpha}^{20^\circ}$ 1·4908, whence $[R_L]_{\alpha}$ 78·9 (calc., 77·00) (Found: C, 65·1; H, 7·5. $C_{16}H_{22}O_5$ requires C, 65·3; H, 7·5%).

This ester (40 g.) was carefully added to a solution of potassium hydroxide (22 g.) in ethyl alcohol (100 c.c.), and the mixture boiled for 2 hours. The alcohol was evaporated, and the solution was acidified with dilute sulphuric acid (22 g. of H_2SO_4 in 200 c.c. of water) and extracted with ether for 1 day in a continuous extractor. The residue after evaporation of the ether from the dried ethereal solution was heated at 170—180° until evolution of carbon dioxide ceased (2 hours); *γ-benzyloxybutyric acid* (25 g.) was then left as a syrupy liquid. This was at once esterified by boiling it for 7 hours with 10% alcoholic sulphuric acid (250 g.). The ester, isolated in the usual manner, had b. p. 163—166°/18 mm. (23 g.; overall yield from the dicarboxylic ester, 76%).

Reduction of Ethyl Benzyloxybutyrate.—The ester was reduced in toluene solution by sodium and ethyl alcohol as described by Marvel and Tanenbaum (*loc. cit.*) in a glass flask with two wide necks down one of which passed the stirrer and the delivery-tube of a dropping-funnel, whilst the other was fitted with the extra-wide metal tube of a long condenser. No difficulty was found in reducing the molten metal to a fine state of division when the stirrer (of the hollow T-piece pattern) was driven directly by an electric motor at high speed. On distillation of the final product, *benzyl δ-hydroxybutyl ether* was obtained (yield 37%) as a colourless oil, b. p. 157°/12 mm., $d_{4^\circ}^{20^\circ}$ (vac.) 1·029, $n_{\alpha}^{20^\circ}$ 1·5107, whence $[R_L]_{\alpha}$ 52·46 (calc., 52·24). It is soluble in alcohol, ether or benzene, but insoluble in water (Found: C, 73·6, 73·5; H, 9·0, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 9·0%). As was the case with the lower homologue (p. 474), the *p*-nitrobenzoate and phenylurethane of this substance could not be obtained crystalline.

Benzyl δ-Chlorobutyl Ether.—Thionyl chloride (6 g.) was gradually added to a well-shaken mixture of benzyl hydroxybutyl ether (9 g.) and dimethylaniline (6 g.), and the product (8 g.; 80% yield) isolated as was the analogous chloropropyl ether (p. 474). *Benzyl chlorobutyl ether* is a pale yellow oil, b. p. 135°/12 mm., $d_4^{20°}$ (vac.) 1·0572, $n_\alpha^{20°}$ 1·5083, whence $[R_L]_\alpha$ 56·10 (calc., 55·56) (Found: Cl, 17·5. $C_{11}H_{15}OCl$ requires Cl, 17·8%).

Benzyl β-Iodoethyl Ether.—Benzyl chloroethyl ether (60 g.) was heated for 30 hours in boiling methyl alcohol with sodium iodide (60 g.), the solvent was then evaporated, and the oil was precipitated by water, removed in ether, dried, and distilled under diminished pressure in a Widmer flask. *Benzyl iodoethyl ether* was thus isolated (yield 60%; some chloro-compound was recovered) as a heavy, colourless oil, b. p. 148—149°/14 mm. (Found: I, 48·0. $C_9H_{11}OI$ requires I, 48·4%).

Experiments with Magnesium β-Benzyloxyethyl Iodide.—Magnesium dissolved readily in an ethereal solution of benzyl iodoethyl ether. (No reaction was observed with the corresponding chloro-compound.) The resulting Grignard reagent was subjected to the action of β-chloroethyl *p*-toluenesulphonate (1 mol.) either in boiling ether or in boiling benzene, but the ester was largely recovered unchanged together with benzyl ethyl ether. The magnesium benzyloxyethyl iodide was also allowed to react in ethereal solution with ethylene oxide, the solution evaporated, and the residue heated; and, lastly, the Grignard reagent in question was added to a mixture of ethylene chlorohydrin with either magnesium phenyl bromide or magnesium ethyl bromide, and the mixture heated. In none of these experiments was benzyl hydroxybutyl ether identified with certainty among the products. In each case benzyl ethyl ether was obtained in quantity.

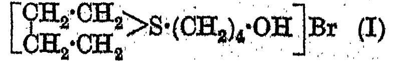
THE UNIVERSITY, SHEFFIELD. [*Received, November 30th*, 1926.]

LXX.—*The Influence of the Sulphur Atom on the Reactivity of Adjacent Atoms or Groups. Part I. A Qualitative Comparison of the Reactivities of Chlorine and Hydroxyl in the α-, β-, γ-, and δ-Positions to a Sulphur Atom.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

THE study of sulphides substituted in the β- and γ-positions having yielded results of great interest (J., 1925, **127**, 2671), we undertook the preparation of a δ-chlorobutyl sulphide. We did not, in fact, succeed in isolating a free δ-chlorobutyl sulphide, owing to the unexpected reactivity of the δ-hydroxy sulphide and to the tendency of the halogenated sulphide to undergo internal salt-formation with production of the tetramethylene sulphide ring. δ-Halogenated butyl sulphides themselves are apparently capable of only a transitory existence. At the same time, the observations made in the course of these experiments provide ample evidence concerning the reactivity of the hydroxyl group in the δ-position.

The method of synthesis proposed was to convert benzyl δ-chlorobutyl ether (see preceding paper) into δδ′-dibenzyloxydibutyl sulphide, $S(CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot O\cdot CH_2Ph)_2$, to remove the benzyl groups by means of hydrobromic acid, and subsequently to convert the resulting dihydroxysulphide into the δδ′-dichlorodibutyl sulphide, $S(CH_2\cdot CH_2\cdot CH_2\cdot CH_2Cl)_2$. In order to test the applicability of the method, and for purposes of comparison, the analogous reactions were first carried out in the γ-substituted propyl series, namely, the conversion of benzyl γ-chloropropyl ether into the sulphide, $S(CH_2\cdot CH_2\cdot CH_2\cdot O\cdot CH_2Ph)_2$, and this into the hydroxy-sulphide, $S(CH_2\cdot CH_2\cdot CH_2\cdot OH)_2$, and γγ′-dichlorodipropyl sulphide, of which the last two compounds had been previously described (*loc. cit.*). This series of reactions proceeded very smoothly to give an excellent yield of the expected chloropropyl sulphide. δδ′-Dibenzyloxydibutyl sulphide was readily obtained from benzyl chlorobutyl ether and hydrobromic acid removed the benzyl groups quantitatively at laboratory temperature; but, although the reaction had been conducted in a manner precisely similar to that successfully adopted for the conversion of γγ′-dibenzyloxydipropyl sulphide into the hydroxypropyl sulphide, the second product of this fission was not dihydroxydibutyl sulphide. The substance obtained proved to be *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide*,



$$\left[\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!S\cdot(CH_2)_4\cdot OH\right]Br \quad (I)$$

which was characterised as the *picrate*, the *bromoplatinate*, and the *bromoaurate*. Confirmation of the structure of this substance was furnished by its ready decomposition by heat with liberation of tetrahydrothiophen.

Whereas a tendency in a δ-halogenated sulphide to ring-closure by internal salt-formation might have been anticipated from analogy with corresponding nitrogen compounds, the rapid substitution of bromine for hydroxyl, which must have preceded it,* was entirely unexpected.

Reactivity of Hydroxyl or Chlorine in the α-, β-, γ-, *and* δ-*Positions Relative to a Sulphur Atom*.—A valid comparison of the reactivities of two compounds can only be made when the reaction involved is the same and proceeds by the same mechanism in the two cases. The reaction of the type $R{\cdot}S{\cdot}(CH_2)_n{\cdot}OH + HCl \rightleftharpoons R{\cdot}S{\cdot}(CH_2)_nCl + H_2O$ which we propose to consider is at least partially reversible, and it seems legitimate, in comparing sulphides substituted in various positions, to make reference to the behaviour of either the hydroxy- or the chloro-sulphide. The high reactivity of both hydroxyl and chlorine in the β-position and the low reactivity of both in the γ-position support this view, which is moreover justifiable from a consideration of the interpretation of this reactivity in terms of electrons (see below). We now include α- and δ-substituted sulphides, therefore, in the comparison, although the evidence refers in the former case only to a chlorosulphide and in the latter to a hydroxysulphide.

It was found by Peters and Walker (*Biochem. J.*, 1923, **17**, 260) that the rate of liberation of acid by hydrolysis in dilute aqueous-alcoholic solution from αα′-dichlorodimethyl sulphide is five times that observed with ββ′-dichlorodiethyl sulphide. Our own experiments, described above, now prove that the hydroxyl group in the δ-position to a sulphur atom has a reactivity with acids of a higher order than that in the γ-position. The reactivities of the hydroxyl group or chlorine atom in these sulphides, with respect to the reactions specified, are therefore related as follows: $\alpha > \beta > \gamma < \delta$.

Interpretation of this Conclusion with Reference to Electronic Theories of Valency.—The markedly higher reactivity of αα′-dichlorodimethyl sulphide and ββ′-dichlorodiethyl sulphide as compared with trimethylene and pentamethylene dichlorides respectively shows that the influence of the sulphur atom is the most important factor involved, any mutual effect of the two chlorine atoms being relatively insignificant.

A high reactivity of the hydroxyl group or of the chlorine atom, with respect to the reaction studied, must depend on an increased negative charge on the oxygen or chlorine atom. Since the carbon chains in these sulphides are saturated, the possibility of an alternating polarity effect need not be considered. The high reactivity of chlorine in the α- and β-positions may be attributed to a general polar effect of the sulphur atom, which, like bivalent oxygen (compare Rây and Robinson, J., 1925, **127**, 1618), tends to repel electrons and thereby increases the negative charge on the chlorine atoms, the effect being greater in the α- than in the β-position owing to the smaller distance of chlorine from sulphur in the former case. In this process, the sulphur atom becomes positively charged to an extent which is presumably increased by the influence of the chlorine atoms in attracting electrons away from it, the reinforcement of the effect of the sulphur atom under the influence of the chlorine atoms being again greatest in the α-chloro-sulphide :

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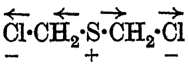
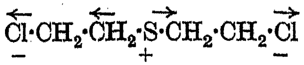
* The only alternative supposition would be the self-addition of the δ-hydroxybutyl sulphide to yield the cyclic sulphonium *base*—a reaction for which we can find no analogy in the chemistry of either sulphur or nitrogen.

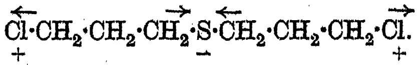


$\underset{-}{\overset{\leftarrow}{\mathrm{Cl}}}\cdot\overset{\leftarrow}{\mathrm{CH_2}}\cdot\underset{+}{\mathrm{S}}\cdot\overset{\rightarrow}{\mathrm{CH_2}}\cdot\underset{-}{\overset{\rightarrow}{\mathrm{Cl}}}$

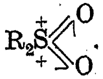


$\underset{-}{\overset{\leftarrow}{\mathrm{Cl}}}\cdot\mathrm{CH_2}\cdot\overset{\leftarrow}{\mathrm{CH_2}}\cdot\underset{+}{\mathrm{S}}\cdot\overset{\rightarrow}{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\underset{-}{\overset{\rightarrow}{\mathrm{Cl}}}$

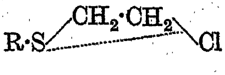
In the case of the γ-chloro-sulphide, these effects will be further diminished owing to the greater distance between sulphur and chlorine. The sulphur atom is here negative (or at least much less positive), and the chlorine atoms are not made reactive :

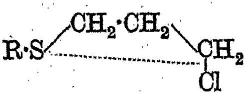


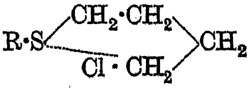
$\underset{+}{\overset{\leftarrow}{\mathrm{Cl}}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\overset{\rightarrow}{\mathrm{CH_2}}\cdot\underset{-}{\mathrm{S}}\cdot\overset{\leftarrow}{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\underset{+}{\overset{\rightarrow}{\mathrm{Cl}}}$.

These conclusions are supported by the variations in the chemical behaviour of the sulphur atom itself. Whereas methiodides of α- or β-chloro-sulphides are unknown—although evidence that methyl iodide and ββ′-dichlorodiethyl sulphide combine to some extent was obtained by Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1229)—we were able to isolate a crystalline derivative of the sulphonium methiodide derived from γγ′-dichlorodipropyl sulphide (Bennett and Hock, *loc. cit.*). A similar gradation in properties of the sulphur atom in these compounds is evident in the ease and extent of their oxidation either to a sulphoxide or to a sulphone, for the sulphoxide of αα′-dichlorodimethyl sulphide and both the sulphoxide and the sulphone of ββ′-dichlorodiethyl sulphide have been described, whilst we found it impossible to isolate the sulphoxide of the γ-chloro-sulphide, the sulphone being formed in all cases. In both these respects, therefore, involving addition of methyl iodide or of oxygen, the reactivity of the sulphur atom varies in the order $\alpha < \beta < \gamma$. This conclusion is exactly what would be expected as a consequence of the electronic distribution already discussed. The sulphur atom in the α- and to a less extent in the β-chloro-sulphide, being already positively charged, will tend to prevent the addition of methyl iodide. The negative nature of the sulphur atom in the γ-chloro-sulphide, on the other hand, explains its oxidation to a sulphone rather than a sulphoxide, since the production of the former gives to the sulphur atom two positive charges instead of one:  $R_2\overset{+}{\underset{+}{S}}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$.

The high reactivity of the hydroxyl group in the δ-position to the sulphur atom is, however, the most interesting result to be considered, since it furnishes definite evidence that the general polar effect, in this case at least, operates chiefly through space rather than along the chain of carbon atoms. For it is clear that if the effect of the sulphur atom on the chlorine or hydroxyl in the γ-position is only slight, its effect on the δ-hydroxyl group, if transmitted exclusively along the chain, must be negligible. At the same time, the rapid transformation of the corresponding halogenated sulphide into the cyclic sulphonium salt (I) provides experimental proof that a substituent in the δ-position does actually approach close to the sulphur atom in space, and the conclusion appears inevitable that the reactivity of the δ-substituent is due to a direct effect of the sulphur atom on it (or on the electron pair binding it to the terminal carbon atom):







It appears to have been widely assumed hitherto that the general polar effect is transmitted either exclusively, or at least principally, along the chain of atoms. Allan, Oxford, Robinson, and Smith, for instance (J., 1926, 406, footnote), mention "possibly also an electrical effect exercised across the intervening space rather than through the chain." Our observations appear to place this possibility beyond doubt. It is probable that the general polar effect, like the alternating effect, is more readily transmitted by an unsaturated than by a saturated chain, there being more freedom of movement of electrons in the former. The chain is saturated in the case under discussion, where the effect through space has now been demonstrated, but a similar effect transmitted through space may be anticipated also where the chain is unsaturated.

EXPERIMENTAL.

γγ′-Dibenzyloxydipropyl Sulphide.—Benzyl γ-chloropropyl ether (9·2 g.) was heated for 6 hours with a solution of sodium sulphide (15 g. of $Na_2S,9H_2O$) in 50% aqueous alcohol (20 c.c.), the mixture poured into water, the oil removed in ether, and the solution washed, dried, and evaporated. The pale yellow oil (7·3 g.) left after heating for an hour at 120° under diminished pressure in a current of air was *γγ′-dibenzyloxydipropyl sulphide*, but did not crystallise and was not analysed. This substance reacted readily with fuming hydrobromic acid in the cold. After the mixture had been kept for 24 hours at the ordinary temperature, the acid and the benzyl bromide which had been produced were removed in a current of steam, and all volatile matter was then driven off by heating under diminished pressure. The residue (3·6 g.) was γγ′-dihydroxydipropyl sulphide, since the action of thionyl chloride (6·4 g.) and dimethylaniline (6·4 g.) readily converted it into the corresponding chloropropyl sulphide, b. p. 150—160°/35 mm. (2·8 g.; 77% yield from the benzyl chloropropyl ether).

δδ′-Dibenzyloxydibutyl Sulphide.—Benzyl δ-chlorobutyl ether (see preceding paper) (9·2 g.) was subjected to the action of aqueous-alcoholic sodium sulphide solution precisely as described above for the corresponding chloropropyl ether, and was thus converted into *δδ′-dibenzyloxydibutyl sulphide* (8 g.), a pale yellow oil which could not be distilled and did not solidify.

Action of Hydrobromic Acid on δδ′-Dibenzyloxydibutyl Sulphide.—Dibenzyloxydibutyl sulphide (8 g.) was covered with 48% hydrobromic acid, hydrogen bromide passed into the cooled mixture to saturation, and the whole kept at the ordinary temperature for 24 hours. A current of steam was passed to remove volatile products, and a heavy oil (7·4 g.) was then collected, b. p. 190—205°, d 1·46, identified as benzyl bromide (b. p. 198°, $d^{15°}$ 1·43; calculated yield, 7·9 g.). The residual aqueous solution was evaporated several times, and with addition of more water, under diminished pressure in order to remove free acid, and finally dried in a current of air under diminished pressure at 100°. The residue left after these operations had been completed was a viscous material readily soluble in cold water, but insoluble in ether or benzene, and by analogy with the corresponding product derived in a similar way from dibenzyloxydipropyl sulphide it was at first assumed to be dihydroxydibutyl sulphide. Yet the action of phenylcarbimide in benzene and of *p*-nitrobenzoyl chloride at 130° yielded no crystalline derivative, diphenylcarbamide and *p*-nitrobenzoic anhydride (m. p. 181°, not depressed by admixture of an authentic specimen) being produced respectively, whereas the dihydroxydipropyl sulphide reacts readily with phenylcarbimide (compare Bennett and Hock, J., 1925, 127, 2673) and it is readily converted, when heated at 130° for 1 hour with *p*-nitrobenzoyl chloride (2 mols.), into *di*-p-*nitrobenzoyloxydipropyl sulphide*, pale yellow needles,

m. p. 104—105°, from benzene–light petroleum (Found: N, 6·4. $C_{20}H_{20}O_8N_2S$ requires N, 6·3%). The residue was also subjected to the action of thionyl chloride (2 mols.) in presence of dimethylaniline and alternatively of pyridine (2 mols.), but no insoluble dichloro-compound was obtained. A closer examination of the substance then showed it to be *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide* (I). Attempts to induce crystallisation or to purify it by precipitation of its solution in ethyl alcohol by ether were unsuccessful. The aqueous solution contained ionic bromine in quantity, and when shaken with freshly-precipitated silver oxide yielded a caustic solution which liberated ammonia from ammonium chloride. With aqueous sodium picrate, a *picrate* was produced which solidified in contact with ethyl alcohol and crystallised in yellow needles, m. p. 189—190°. Heated at 250° with nitric acid and silver nitrate in a sealed tube, it yielded no silver bromide. Owing to an unexpected transformation of the sulphonium bromide on keeping for several weeks (see p. 483), no analysis of this picrate could be made.

Precipitation of the aqueous acetone or alcoholic solution of the sulphonium bromide with mercuric bromide under various conditions gave white solids of m. p. 110—135° and 150—200°, which did not seem to be definite chemical individuals and were not further examined. The *bromoplatinate* is a buff, microcrystalline powder insoluble in water and most organic solvents but readily soluble in glycerol-α-dichlorohydrin, and decomposes without melting at 165—170° (Found: Pt, 19·4, 19·2; Br, 49·7. $C_{16}H_{34}O_2Br_6S_2Pt$ requires Pt, 19·6; Br, 48·1%). The *bromoaurate* was precipitated from aqueous solution as a viscous mass which then solidified to a reddish-purple solid; after being washed with water and ether, and dried at the ordinary temperature, it melted with decomposition at 65—70° (Found: Au, 28·9; Br, 48·4. $C_8H_{17}OBr_4SAu$ requires Au, 29·1; Br, 47·3%).

When the dibenzyloxydibutyl sulphide (2 g.) and saturated hydrobromic acid (3·5 g.) were heated together in a sealed tube at 120—150° for 6 hours, the products were identical with those obtained when the reaction occurred at the ordinary temperature. The picrate, m. p. 190°, was readily obtained pure and shown to be identical with the picrate described above, and it was again found to be free from bromine.

Decomposition of Tetrahydrothiophen-δ-hydroxybutylsulphonium Bromide by Heat.—When the crude sulphonium bromide was heated, it decomposed readily, the products being almost entirely of a volatile nature. Some two-thirds of the distillate collected during the operation had b. p. 110—135°, and the remainder had b. p.

140—185°. The former fraction, which had an unpleasant odour, was separated from a little water and dried, and was then identified as tetrahydrothiophen (tetramethylene sulphide) by the preparation of its methiodide, m. p. 195—197° (decomp.) (Found: I, 54·4. Calc.: I, 55·1%) (v. Braun and Trümpler, *Ber.*, 1910, **43**, 547, give the b. p. of tetrahydrothiophen as 119° and the m. p. of the methiodide as 185—190°), its mercurichloride, m. p. 125—128° (decomp.) [Grischkevitch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 901, gives 124·5—125·5° (decomp.): recrystallisation of this mercurichloride raised the m. p. to 127—133° (decomp.), but the smell of the parent sulphide was evident in the mother-liquor], and the *bromoplatinate*, an orange-red solid darkening at 230° and decomposing at 236—238° (Found: Pt, 28·5; Br, 45·8. $C_8H_{10}Br_4S_2Pt$ requires Pt, 28·2; Br, 46·2%).

Tetrahydrothiophen-δ-bromobutylsulphonium Bromide.—It was found that this substance had been unexpectedly produced from a sample of the δ-hydroxybutylsulphonium bromide which, without having been completely freed from hydrobromic acid, had been left for several weeks in a desiccator. When this was converted into its picrate, the oily substance would not crystallise on inoculation with the picrate of m. p. 190°, but it finally solidified at 0° and after eight crystallisations from ethyl alcohol, *tetrahydrothiophen-δ-bromobutylsulphonium picrate* was obtained as bright yellow needles, m. p. 92—96°, quite distinct from the picrate of m. p. 190° described above (Found: C, 36·7; H, 4·3; Br, 16·6. $C_{14}H_{18}O_7N_3BrS$ requires C, 37·2; H, 4·0; Br, 17·7%). This picrate decomposed when kept for a few days at the ordinary temperature (compare the decomposition of dimethyl-β-hydroxyethylsulphonium iodide, Renshaw, Bacon, and Roblyer, *J. Amer. Chem. Soc.*, 1926, **48**, 517). Its production is not easily accounted for in view of the fact that it was not formed in the experiment described above where the reaction was conducted in a sealed tube at 100°. It is conceivable, however, that its isolation in this case may be due to the partial dissociation of the hydroxybutylsulphonium bromide, the conversion of the δ-bromobutyl alcohol liberated into αδ-dibromobutane, and recombination of the latter with the tetrahydrothiophen to yield a bromobutylsulphonium salt.

We wish once more to express our thanks to the West Riding County Council for a scholarship which has enabled one of us (A. L. H.) to take part in the investigation recorded in this and the preceding paper, and to the Chemical Society for a grant which has defrayed some of the expense involved.

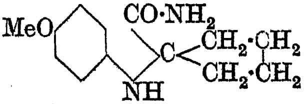
THE UNIVERSITY, SHEFFIELD. [*Received, November 30th,* 1926.]

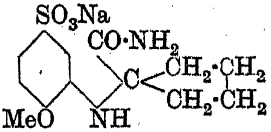
LXXI.—*The Condensation of Substituted Anilines with* cyclo*Pentanone Cyanohydrin. Derivatives of 1-Anilino*cyclo*pentane-1-carboxylic Acid.*

By Stephen Hellicar Oakeshott and Sydney Glenn Preston Plant.

It has already been shown that 1-anilino*cyclo*pentane-1-carboxylic acid and the corresponding 1-*p*-toluidino-compound give carbazole and 3-methylcarbazole, respectively, on fusion with a mixture of potassium hydroxide and sodium ethoxide (Plant and Facer, J., 1925, **127**, 2037; Oakeshott and Plant, J., 1926, 1210). With a view to extend this reaction and establish the structures of some carbazole compounds, the preparation of a number of derivatives of 1-anilino*cyclo*pentane-1-carboxylic acid has been investigated. The general method of procedure has been to prepare the corresponding nitrile by mixing the required amine with *cyclo*pentanone (rather more than 1 mol.) in glacial acetic acid with the subsequent addition of aqueous potassium cyanide (about 1¼ mols.) (compare the preparation of 1-anilino-1-cyano*cyclo*hexane, Walther and Hübner, *J. pr. Chem.*, 1916, **93**, 124). The direct hydrolysis of the nitrile to the corresponding acid in several cases was difficult, but an almost quantitative conversion could be obtained if the nitrile was first converted into the amide and subsequently into the acid. It was observed in some instances that the nature and position of the substituent in the aniline molecule considerably retarded the formation of the corresponding nitrile, and a detailed study of this was undertaken. The presence of a methyl or methoxyl group in the benzene ring, whatever its position with respect to the amino-group, did not influence the condensation, the reaction being completed during the course of an hour at room temperature. The nitro-group had the greatest effect, this being most pronounced when the nitro-group was in the ortho-position, and least when it was in the meta-position, to the amino-group. Thus *o*-nitroaniline could not be made to condense at all, even when the mixture was heated in a sealed tube at 100° for 5 days, *p*-nitroaniline reacted during 2 days if the temperature was kept at 40—45°, while the reaction with *m*-nitroaniline took place slowly at room temperature, several hours being required for its completion. The effect of the carboxyl group was similar, but not so pronounced, anthranilic acid requiring a few days at 40—45°, *p*-aminobenzoic acid 24 hours at this temperature, whilst *m*-aminobenzoic acid reacted completely in a few hours at room temperature. The retarding effect of chlorine and bromine was negligible, except when the group was ortho to the amino-group, in which case several hours were required at room temperature for the completion of the reaction.

The formation of the amide from the corresponding nitrile proceeded smoothly, by keeping in concentrated sulphuric acid solution for 2 days, in all cases except some in which a methoxyl group was present. It was possible to convert 1-p-*anisidino*-1-*cyano*cyclo*pentane* into the *amide* (I), but with the corresponding o-*anisidino*- and m-*anisidino*-compounds sulphonation took place at the same time. From 1-o-*anisidino*-1-*cyano*cyclo*pentane* the sodium salt of a monosulphonic acid was isolated, and, since no apparent sulphonation takes place with the *p*-anisidino-compound or in the absence of the methoxyl group, it seems certain that the sulphonyl group enters the position para to the methoxyl group to give *sodium* 1-o-*anisidino*cyclo*pentane*-1-*carboxyamide*-5′-*sulphonate* (II).

(I.) 

 (II.)

1-*Veratrylamino*-1-*cyano*cyclo*pentane* and 1-mm′-*dimethoxyanilino*-1-*cyano*cyclo*pentane* were prepared from veratrylamine and 3 : 5-*dimethoxyaniline*, respectively, in order to investigate the possibility of obtaining the corresponding dimethoxy-derivatives of ψ-indoxyl-*spirocyclo*pentane (compare Perkin and Plant, J., 1923, **123**, 676) by interaction of the cyano-group and the hydrogen atom in the ortho-position in the benzene nucleus under conditions similar to those used by Hoesch (*Ber.*, 1915, **48**, 1122) for condensing nitriles with certain hydroxybenzene compounds. Several attempts to bring about this reaction in dry ether in the presence of zinc chloride or aluminium chloride and dry hydrogen chloride were unsuccessful, the nitriles being recovered unchanged. The failure of this reaction may be accounted for by the absence of an unmethylated hydroxyl group in the benzene nucleus or by the basic nature of the substance.

Fusion of 1-o-*toluidino*cyclo*pentane*-1-*carboxylic acid* with a mixture of potassium hydroxide and sodium ethoxide has given rise to 1-methylcarbazole, which was identified by comparison with a specimen of 1-methylcarbazole prepared by oxidising 8-methyltetrahydrocarbazole. The fact that this fusion gives rise to 1-methylcarbazole and not to 1 : 8-dimethylcarbazole confirms our previous evidence for the view that the formation of carbazole from 1-anilino*cyclo*pentane-1-carboxylic acid involves the enlargement of the *cyclo*pentane ring (*loc. cit.*).

EXPERIMENTAL.

1-o-*Toluidino*cyclo*pentane*-1-*carboxylic Acid.*—*o*-Toluidine (27·5 g.) and *cyclo*pentanone (21 g.) were mixed in glacial acetic acid (200 c.c.) and then treated at room temperature with potassium cyanide (20 g.), dissolved in water (60 c.c.). After a short time, the product separated as an oil which, on stirring, solidified, and, after crystallisation from low-boiling petroleum, 1-o-*toluidino*-1-*cyano*cyclo*pentane* was obtained in good yield as colourless prisms, m. p. 68°. A solution of this in concentrated sulphuric acid was kept for 2 days and poured on to ice, and the liquid made alkaline with ammonia. 1-o-*Toluidino*cyclo*pentane*-1-*carboxyamide*, which was precipitated, separated from petroleum in colourless prisms, m. p. 122°. The amide, on being rubbed with concentrated hydrochloric acid, gave its *hydrochloride*, which was added to an excess of hydrochloric acid and the mixture boiled to dryness. The residue was dissolved in aqueous sodium hydroxide, and the filtered solution treated with an excess of glacial acetic acid. This precipitated 1-o-*toluidino*cyclo*pentane*-1-*carboxylic acid*, which separated from xylene in colourless needles, m. p. 128° (Found: N, 6·5. $C_{13}H_{17}O_2N$ requires N, 6·4%). The acid was unaltered by heating with an excess of potassium hydroxide up to 300°. From an aqueous solution of the cooled mixture, the substance was recovered by the addition of acetic acid.

1-*Methylcarbazole.*—1-*o*-Toluidino*cyclo*pentane-1-carboxylic acid (16 g.) was mixed with potassium hydroxide (35 g.) and sodium ethoxide (40 g.) and heated from 270° to 320° during ½ hour. After cooling, the pulverised product was treated with water, and the insoluble portion dried and distilled. The colourless distillate was crystallised from petroleum, 1-methylcarbazole separating in colourless plates, m. p. 117° (compare Ullmann, *Annalen*, 1903, **332**, 87). Its picrate separated from hot alcohol in scarlet needles, m. p. 144° (compare Ullmann, *loc. cit.*). The 1-methylcarbazole obtained in this way dissolved in concentrated sulphuric acid to give a pale green solution, the colour of which faded in 30 seconds to straw-yellow. The addition of a drop of concentrated nitric acid to this solution produced an intense green colour.

1-Methylcarbazole was also synthesised in the following way: *o*-Tolylhydrazine (12·2 g.) and *cyclo*hexanone (9·8 g.) were heated together on the steam-bath for a short time, and, on cooling, *cyclo*hexanone-*o*-tolylhydrazone was obtained as a solid mass. The crude hydrazone was heated to boiling with dilute sulphuric acid for a few minutes; the 8-methyltetrahydrocarbazole which separated crystallised from aqueous alcohol in colourless plates, m. p. 98°. 8-Methyltetrahydrocarbazole has previously been prepared by the interaction of chloro*cyclo*hexanone and *o*-toluidine, and found to melt at 98° (D.R.-P. 374,098). A solution of 8-methyltetrahydrocarbazole (6 g.) and sulphur (2·1 g.) in pure quinoline (20 c.c.) was boiled for 20 minutes and then poured into a mixture of dilute hydrochloric acid and ice. The oil which separated gradually solidified, and was collected, dried, and distilled with an equal volume of iron powder. The distillate, m. p. 110°, was converted into its picrate, which separated from hot alcohol in scarlet needles, m. p. 144°. On warming the picrate with aqueous sodium hydroxide, 1-methylcarbazole, m. p. 117°, was obtained. The fact that this product was identical with that obtained from 1-*o*-toluidino*cyclo*pentane-1-carboxylic acid was established by a mixed m. p. determination, by the colour changes in concentrated sulphuric acid solution, and by the melting points of their picrates.

1-m-*Toluidino*cyclo*pentane*-1-*carboxylic Acid.*—*m*-Toluidine (10 c.c.) and *cyclo*pentanone (8·5 c.c.), dissolved in glacial acetic acid (50 c.c.), were treated at room temperature with potassium cyanide (7 g.), in a little water; an oily product gradually separated. After 2 hours, the mixture was poured into an excess of water, the oily nitrile gradually solidified, and 1-m-*toluidino*-1-*cyano*cyclo*pentane* was obtained as a colourless solid, m. p. 53°, on rubbing with petroleum. This nitrile was hydrolysed in the same way as the corresponding *o*-toluidino-compound and the 1-m-*toluidino*cyclo*pentane*-1-*carboxyamide* obtained separated from aqueous alcohol in colourless prisms, m. p. 145°. The clear solution of the amide in concentrated hydrochloric acid was boiled under reflux for 1 hour and evaporated to dryness, the residue was dissolved in aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. The product was crystallised from aqueous alcohol and 1-m-*toluidino*cyclo*pentane*-1-*carboxylic acid* obtained in colourless needles, m. p. 123—124° (Found: N, 6·5. $C_{13}H_{17}O_2N$ requires N, 6·4%).

Condensation of the Methoxyanilines with cyclo*Pentanone Cyanohydrin.*

1-o-*Anisidino*-1-*cyano*cyclo*pentane.*—The reaction mixture was kept at room temperature for 2 hours and then poured into water, the oily product was extracted with ether, and the ethereal solution shaken twice with water and then with dilute aqueous sodium carbonate. On drying the solution with calcium chloride and removing the ether, 1-o-*anisidino*-1-*cyano*cyclo*pentane* remained as a brown syrup. Its solution in concentrated sulphuric acid was kept for 2 days and then poured into ice-water. Calcium carbonate was added to the hot solution until effervescence ceased, and, after filtering, it was treated with a slight excess of sodium carbonate to precipitate the calcium, again filtered, and evaporated to dryness. The residue was extracted with hot alcohol, acetone was added to the clear alcoholic solution, and, on standing, *sodium* 1-o-*anisidino*cyclo*pentane*-1-*carboxyamide*-5′-*sulphonate* separated in colourless prisms (Found: S, 9·6. $C_{13}H_{17}O_5N_2SNa$ requires S, 9·5%). This sodium salt is very soluble in water.

1-m-*Anisidino*-1-*cyano*cyclo*pentane*.—From the reaction mixture at room temperature, the oily product gradually separated during 1 hour. After dilution with water, the oil solidified on being rubbed with alcohol, and, on crystallisation from this solvent, 1-m-*anisidino*-1-*cyano*cyclo*pentane* separated in colourless prisms, m. p. 132°. The solution of this product in concentrated sulphuric acid became dark green, and was poured into ice-water after 2 days; from the intense purple solution produced, nothing separated on addition of ammonia.

1-p-*Anisidino*cyclo*pentane*-1-*carboxylic Acid*.—The reaction mixture was treated as described for *o*-anisidine, 1-p-*anisidino*-1-*cyano*cyclo*pentane* being obtained as a brown syrup. By treatment with concentrated sulphuric acid for 2 days, pouring into ice-water, making alkaline with ammonia, and crystallising the product from benzene–petroleum, 1-p-*anisidino*cyclo*pentane*-1-*carboxyamide* was obtained in almost colourless prisms, m. p. 81—82°. The amide was hydrolysed by boiling its clear solution in concentrated hydrochloric acid for ½ hour; this was then evaporated to dryness, the residue dissolved in dilute aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. 1-p-*Anisidino*cyclo*pentane*-1-*carboxylic acid* separates from alcohol in colourless prisms, m. p. 160° (Found: N, 6·0. $C_{13}H_{17}O_3N$ requires N, 5·9%).

1-*Veratrylamino*-1-*cyano*cyclo*pentane*.—From the reaction mixture, after a short time, the addition of ammonia precipitated 1-*veratrylamino*-1-*cyano*cyclo*pentane*, which separated from benzene–petroleum in colourless plates, m. p. 98° (Found: N, 11·3. $C_{14}H_{18}O_2N_2$ requires N, 11·4%). When this nitrile dissolves in concentrated sulphuric acid, sulphonation apparently takes place, since dilution of the solution after 2 days and treatment with ammonia gives no precipitate.

1-mm′-*Dimethoxyanilino*-1-*cyano*cyclo*pentane*.—3 : 5-Dimethoxynitrobenzene was obtained from trinitrobenzene by the steps described by Vermeulen (*Rec. trav. chim.*, 1906, **25**, 26), although the following conditions for the methylation of 5-nitro-3-hydroxyanisole were found to be more satisfactory than those given. The anisole (8 g.), methyl sulphate (7·4 g.), and potassium carbonate (8 g.) were mixed in toluene (200 c.c.) and boiled for 4 hours. The toluene was removed in steam and, on cooling the residue, 3 : 5-dimethoxynitrobenzene solidified; after recrystallisation from ethyl acetate, it melted at 89°.

The most convenient conditions for reducing this compound are similar to those used by Hope and Robinson (J., 1911, 99, 1159) for reducing anhydrocotarnine-5-nitrophthalide. 3 : 5-Dimethoxynitrobenzene (10 g.) was dissolved in a mixture of glacial acetic acid (100 c.c.) and water (100 c.c.), tin (1 g.) was added, followed by a solution of stannous chloride (6 g.) in hydrochloric acid (60 c.c.), the mixture being then stirred vigorously and maintained at 40° for a few hours. After being made alkaline with sodium hydroxide, the product was extracted with ether and the ethereal solution was shaken with water and dried over sodium sulphate. The ether was removed, and 3 : 5-*dimethoxyaniline* (3·5 g.) obtained on distillation, b. p. 178°/20 mm. On treating the amine with an excess of acetic anhydride and then mixing the product with benzene–petroleum, a solid was obtained. This was crystallised from water, 3 : 5-*dimethoxyacetanilide* separating in colourless needles, m. p. 157° (Found : N, 7·3. $C_{10}H_{13}O_3N$ requires N, 7·2%).

A mixture of 3 : 5-dimethoxyaniline (5 g.), *cyclo*pentanone (3 c.c.), and concentrated aqueous potassium cyanide (3 g.) in glacial acetic acid (30 c.c.), after standing at room temperature for a short time, was partly neutralised with ammonia. The dark-coloured oil that separated was extracted with ether, the extract was twice shaken with water and dried over sodium sulphate, and the solvent removed. The dark oily residue was obtained in colourless plates after successive treatments with low-boiling petroleum. 1-mm'-*Dimethoxyanilino*-1-*cyano*cyclo*pentane* melts at 150° (Found : N, 11·1. $C_{14}H_{18}O_2N_2$ requires N, 11·4%).

Condensation of the Chloroanilines with cyclo*Pentanone Cyanohydrin.*

1-o-*Chloroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was left at room temperature for 12 hours, and then poured into dilute hydrochloric acid to remove any unchanged *o*-chloroaniline, but the oily product which separated did not solidify after several hours. The mixture was shaken with ether and the ethereal solution was washed with water and dilute aqueous sodium carbonate and dried over calcium chloride. After removal of the ether, 1-o-*chloroanilino*-1-*cyano*cyclo*pentane* remained as a yellow oil. This was dissolved in concentrated sulphuric acid and the solution was kept for 2 days and poured on to ice. Dilution with water, without the addition of ammonia, caused the separation of the product as a sticky solid, which hardened on being rubbed with petroleum. After crystallisation from petroleum, 1-o-*chloroanilino*cyclo*pentane*-1-*carboxyamide* was obtained in colourless prisms,

m. p. 113° (Found: N, 11·6. $C_{12}H_{15}ON_2Cl$ requires N, 11·7%). The amide was hydrolysed by boiling its solution in concentrated hydrochloric acid for an hour, and the product isolated by the method employed in the previous cases. After crystallisation from aqueous alcohol, 1-o-*chloroanilino*cyclo*pentane*-1-*carboxylic acid* was obtained in colourless needles, m. p. 145° (Found: N, 5·8. $C_{12}H_{14}O_2NCl$ requires N, 5·8%).

1-m-*Chloroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept for 1 hour at room temperature and then poured into water; the product separated as an oil which slowly solidified on stirring. After crystallisation from low-boiling petroleum, 1-m-*chloroanilino*-1-*cyano*cyclo*pentane* was obtained in colourless prisms, m. p. 47°. Its solution in concentrated sulphuric acid, after 2 days, was poured on to ice, and the product isolated by making it alkaline with ammonia; the 1-m-*chloroanilino*cyclo*pentane*-1-*carboxyamide* obtained crystallised from aqueous alcohol in colourless prisms, m. p. 118°. A solution of this in concentrated hydrochloric acid was boiled for ½ hour, the product isolated as before, and, after crystallisation from aqueous alcohol, 1-m-*chloroanilino*cyclo*pentane*-1-*carboxylic acid* was obtained in colourless prisms, m. p. 112° (Found: N, 5·8. $C_{12}H_{14}O_2NCl$ requires N, 5·8%).

1-p-*Chloroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was treated exactly as described for *m*-chloroaniline, and the condensation was complete after 15 minutes. From aqueous alcohol, 1-p-*chloroanilino*-1-*cyano*cyclo*pentane* separated in long, colourless prisms, m. p. 73°. The hydrolysis of this nitrile proceeded exactly as with the *m*-chloroanilino-compound; the 1-p-*chloroanilino*cyclo*pentane*-1-*carboxyamide* obtained crystallised from aqueous alcohol in colourless needles, m. p. 132°. 1-p-*Chloroanilino*cyclo*pentane*-1-*carboxylic acid* crystallised from benzene in colourless prisms, m. p. 144° (Found: N, 5·5. $C_{12}H_{14}O_2NCl$ requires N, 5·8%).

Condensation of the Bromoanilines with cyclo*Pentanone Cyanohydrin.*

1-o-*Bromoanilino*cyclo*pentane*-1-*carboxylic Acid.*—The preparation of this acid followed exactly the same course as that described for the *o*-chloroanilino-derivative. 1-o-*Bromoanilino*-1-*cyano*cyclo*pentane* was obtained as a yellowish-brown oil, but its complete formation required about 24 hours at room temperature. 1-o-*Bromoanilino*cyclo*pentane*-1-*carboxyamide* separated from petroleum in colourless prisms, m. p. 128°, and 1-o-*bromoanilino*cyclo*pentane*-1-*carboxylic acid* from aqueous alcohol in colourless prisms, m. p. 140° (Found: N, 4·9. $C_{12}H_{14}O_2NBr$ requires N, 4·9%).

1-m-*Bromoanilino*cyclo*pentane*-1-*carboxylic Acid.*—The formation of 1-m-*bromoanilino*-1-*cyano*cyclo*pentane* took place under the conditions described for the corresponding *m*-chloroanilino-compound, but the product separated as an oil and, after extraction with ether, it was ultimately obtained as a yellowish-brown syrup. 1-m-*Bromoanilino*cyclo*pentane*-1-*carboxyamide* separated from aqueous alcohol in colourless plates, m. p. 126°, and 1-m-*bromoanilino*cyclo*pentane*-1-*carboxylic acid* in colourless needles, m. p. 130° (Found: N, 4·9. $C_{12}H_{14}O_2NBr$ requires N, 4·9%).

1-p-*Bromoanilino*cyclo*pentane*-1-*carboxylic Acid.*—The formation of this compound followed the course described for the *p*-chloroanilino-derivative. 1-p-*Bromoanilino*-1-*cyano*cyclo*pentane* separated from petroleum in colourless plates, m. p. 69°, 1-p-*bromoanilino*cyclo*pentane*-1-*carboxyamide* from aqueous alcohol in colourless plates, m. p. 145°, and 1-p-*bromoanilino*cyclo*pentane*-1-*carboxylic acid* from aqueous alcohol in colourless prisms, m. p. 130° (Found: N, 5·2. $C_{12}H_{14}O_2NBr$ requires N, 4·9%).

Condensation of the Nitroanilines with cyclo*Pentanone Cyanohydrin.*

1-m-*Nitroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The appropriate mixture was kept at room temperature, the course of the reaction being followed by taking advantage of the fact that *m*-nitroaniline dissolves in dilute hydrochloric acid, whilst the condensation product remains undissolved. On pouring the product into water after 1 hour, it was found that about 80% of the mixture was unchanged *m*-nitroaniline; but after 18 hours the reaction had proceeded practically to completion. 1-m-*Nitroanilino*-1-*cyano*cyclo*pentane* separates from aqueous alcohol in yellow prisms, m. p. 95° (Found: N, 18·0. $C_{12}H_{13}O_2N_3$ requires N, 18·2%). The hydrolysis of this nitrile was carried out in the usual way, and the 1-m-*nitroanilino*cyclo*pentane*-1-*carboxyamide* obtained separated from aqueous alcohol in orange prisms, m. p. 144° (Found: N, 16·8. $C_{12}H_{15}O_3N_3$ requires N, 16·9%). 1-m-*Nitroanilino*cyclo*pentane*-1-*carboxylic acid* was obtained, after crystallisation from aqueous alcohol, in long, yellow prisms, m. p. 137° (Found: N, 11·4. $C_{12}H_{14}O_4N_2$ requires N, 11·2%).

1-p-*Nitroanilino*cyclo*pentane*-1-*carboxylic Acid.*—As in the case of the *m*-nitroanilino-derivative, the course of the condensation may be followed easily, since the product is insoluble in dilute hydrochloric acid, in which *p*-nitroaniline dissolves. After standing at room temperature for 15 hours, the mixture had undergone very little change, the product being almost entirely soluble in dilute hydrochloric acid. When the reaction mixture was kept in a water-bath at 40—45°, 1-p-*nitroanilino*-1-*cyano*cyclo*pentane* gradually separated in yellow plates during 2 days. A further quantity of the nitrile was obtained by diluting the mother-liquor with water and crystallising the product from glacial acetic acid. The nitrile separated from this solvent in yellow plates, m. p. 165° (Found: N, 18·2. $C_{12}H_{13}O_2N_3$ requires N, 18·2%). 1-p-*Nitroanilino*cyclo*pentane*-1-*carboxyamide* was obtained by pouring a solution of this nitrile in concentrated sulphuric acid into water after 2 days, without making it alkaline, and separated from alcohol in yellow plates, m. p. 231°. 1-p-*Nitroanilino*cyclo*pentane*-1-*carboxylic acid*, obtained in the usual way, separated from aqueous alcohol in yellow plates, m. p. 187° (Found: N, 11·2. $C_{12}H_{14}O_4N_2$ requires N, 11·2%).

Condensation of the Aminobenzoic Acids with cyclo*Pentanone Cyanohydrin.*

The Amide of 1-o-*Carboxyanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept for 5 days at 40—45°, and poured into water, and the solid product crystallised from benzene–petroleum, from which 1-o-*carboxyanilino*-1-*cyano*cyclo*pentane* separated in colourless needles, m. p. 122°. Its solution in concentrated sulphuric acid, after being kept for 2 days and then poured into much ice-water, yielded the *amide* of 1-o-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid*, which separated from alcohol in colourless prisms, m. p. 225° (after prolonged drying). An attempt to hydrolyse this amide to the corresponding acid by boiling with concentrated hydrochloric acid for 1 hour and isolating the product in the usual way yielded 1-anilino*cyclo*pentane-1-carboxylic acid, m. p. 160—161° (compare Plant and Facer, *loc. cit.*). The identity of this acid was established by analysis (Found: N, 7·0. Calc.: N, 6·8%) and by a mixed m. p. determination. Other attempts to obtain 1-*o*-carboxyanilino*cyclo*pentane-1-carboxylic acid have so far been unsuccessful.

The Amide of 1-m-*Carboxyanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept for 4 hours at room temperature, and the product was isolated by pouring the mixture into water, *m*-aminobenzoic acid being soluble in dilute acetic acid. After crystallisation from toluene, 1-m-*carboxyanilino*-1-*cyano*cyclo*pentane* was obtained in colourless needles, m. p. 153°. The solution of the nitrile in concentrated sulphuric acid was kept for 2 days and poured into ice-water, and the mixture was made alkaline with ammonia and then acidified with acetic acid; the *amide* of 1-m-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid* that separated crystallised from water in colourless prisms, m. p. 215° (Found: N, 11·2. $C_{13}H_{16}O_3N_2$ requires N, 11·3%).

When the amide (20 g.) was heated with a mixture of potassium hydroxide (36 g.) and sodium ethoxide (40 g.) at 270—320° for ½ hour and the product, after cooling, was treated with water, a small quantity of carbazole remained. This was distilled and subsequently crystallised from toluene and was then identified by a mixed m. p. determination and by conversion into its picrate, m. p. 186°.

1-p-*Carboxyanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept at 40°, and, during the course of 24 hours, colourless prisms separated. After recrystallisation from glacial acetic acid, 1-p-*carboxyanilino*-1-*cyano*cyclo*pentane* was obtained in colourless prisms, m. p. 189—190°. Hydrolysis was carried out as described for the *m*-carboxyanilino-derivative and, on crystallisation from alcohol, the *amide* of 1-p-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid* separated in colourless prisms, m. p. 272°. The formation of the acid proceeded in the usual way and 1-p-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid* was obtained, after crystallisation from aqueous alcohol, in colourless prisms, m. p. 225° (decomp.) (Found: N, 5·6. $C_{13}H_{15}O_4N$ requires N, 5·6%).

The authors wish to express their thanks to Mr. F. C. Hall for carrying out the analyses given in this paper.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, December 21st,* 1926.]

LXXII.—*Pseudo-ternary Systems containing Sulphur. Part II. The System Sulphur–Benzoic Acid.*

By DALZIEL LLEWELLYN HAMMICK and WINSTON E. HOLT.

KRUYT (*Z. physikal. Chem.*, 1909, **67**, 330) observed that when mixtures of sulphur and benzoic acid are heated slowly, a cloud (new liquid phase) appears in the sulphur-rich layer in the neighbourhood of 170° and disappears on still further raising the temperature. This behaviour is what would be expected if the solubility curve for liquid sulphur in liquid benzoic acid became retrograde in the neighbourhood of 170° and at higher temperatures resumed its original direction, *i.e.*, if the miscibility curve for liquid sulphur and benzoic acid were of the Type η predicted by Kruyt as one of the possible types for pseudo-ternary systems containing sulphur (compare *ibid.*, **65**, 486). Kruyt, however, rejects this explanation on the grounds that according to his experiments the solubility of benzoic acid in liquid sulphur increases slightly with temperature in the region where the clouding effect occurs. Further, he claims that at about 170° the solubility of benzoic acid increases from

2·2% when the two phases are left in contact for a few minutes to 2·8% when they remain together for 5—10 hours. He concludes that in the neighbourhood of 170° three liquid layers can coexist, *viz.*, a solution of sulphur in benzoic acid, a solution of benzoic acid in a liquid sulphur that is mainly S_λ, and a second solution of benzoic acid in a liquid sulphur that is mainly S_μ.

We have determined equilibria in the system sulphur–benzoic acid by the synthetic method used in our previous investigations on sulphur systems (J., 1926, 1995). Weighed quantities of pure sulphur and benzoic acid (m. p. 121·7°) were sealed in bulb tubes and the necks drawn out to long spindles so that the melted contents could be well mixed by rotating the spindles. Equilibrium temperatures were determined by observing the formation and disappearance, in a regulated thermostat, of the cloud of droplets constituting a second liquid phase. The sulphur-rich phases at lower temperatures contain quantities of benzoic acid of the order of 2%, and, as will be seen from Fig. 1, their composition varies with temperature in a complicated way within a very small range of concentrations. Consequently the mixtures had to be made up with the greatest care. The benzoic acid was introduced into the bulbs first, so that any particles adhering to the walls would be swept in by the large excess of sulphur that was introduced next. The loss in weight that occurred on sealing the bulbs was found to be practically constant at 0·001 g. The contents of the bulbs weighed from 4 to 7 g.

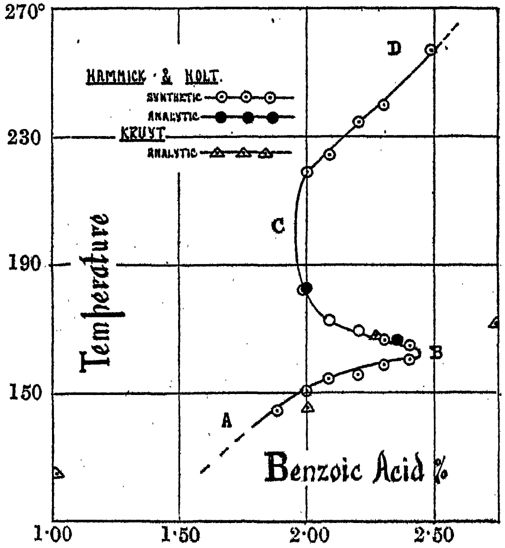
The results obtained are given in Table I; T_1 denotes the temperatures at which heterogeneous liquid mixtures of sulphur and benzoic acid first become homogeneous. On raising the temperature to T_2, the mixture again becomes heterogeneous; at still higher temperatures, it becomes dark and viscous and finally clears again at temperature T_3. The accuracy of temperatures T_1 and T_2 is about ±1°; the final clearing temperatures, T_3, are much more difficult to observe, but are probably correct to ±2°. All the values of T quoted are means of several observations made with rising and falling temperatures.

TABLE I.

Benzoic acid (%) ...	1·89	2·00	2·09	2·20	2·30	2·40	2·49
T_1	145°	151°	154·5°	156°	159·5°	161·5°	—
T_2	—	183	173	170	167·3	165	—
T_3	—	219	225	235	—	242	257·5°

The above results are plotted in Fig. 1, and it will at once be seen that the diagram gives an explanation of the clouding phenomena observed by Kruyt. Most of his mixtures contained considerable percentages of benzoic acid, and hence, at all temperatures below the critical solution temperature, he had two liquid layers present. On heating such a mixture, separation of the benzoic-acid-rich phase in the sulphur layer will take place directly the point of inflexion B in Fig. 1 is passed. Owing to the viscosity of the sulphur-rich layer, the separated droplets will not at once coalesce with the benzoic acid layer, but will finally disappear at higher temperatures at some point along the curve CD. Any mixture of sulphur and benzoic acid on cooling from high temperatures will show a clouding effect directly the conditions represented by the curve CD or its prolongation are reached. Between 165° and 175° reabsorption of part or all of the cloud of droplets will

FIG. 1.



occur. When mixtures in which the amounts of benzoic acid lie between 2·0% and 2·4% are used, the above phenomena are more clearly defined and more readily controlled. For instance, a mixture containing 2·30% of benzoic acid is homogeneous at 250°; on cooling, turbidity occurs at about 240° and persists until 167° is reached. The mixture becomes homogeneous again whilst the temperature drops to 159°. The heterogeneous region is now re-entered and the liquid clouds. In short, the sulphur-rich side of the diagram for the system is of the type predicted by Kruyt (*loc. cit.*) as possible in pseudo-ternary sulphur systems, and it is not necessary, in order to account for the clouding phenomena, to suppose that three liquid layers coexist in equilibrium in the neighbourhood of 170°.

There remains, however, the question of the increase in solubility of benzoic acid in liquid sulphur indicated by Kruyt's experiments between 170° and 185° in direct contradiction to our results obtained by the synthetic method. We have therefore made direct analyses of the sulphur layers at 169° and 183°. Mixtures containing roughly equal quantities of sulphur and benzoic acid and weighing 7—8 g. were enclosed in sealed tubes for 4, 8, and 12 hours, respectively, in the vapour of a specimen of phenetole of b. p. 169°. The tubes were rapidly cooled and allowed to stand over-night. They were then opened and about 1 g. of the solid sulphur layer removed. This was dissolved in carbon disulphide and titrated with $N/100$-sodium hydroxide after the addition of alcohol. The percentages of benzoic acid found in the sulphur layer were 2·25, 2·35, and 2·30. Similarly, a mixture kept in the vapour of boiling aniline (183°) for 8 hours gave a sulphur layer containing 2·04% of benzoic acid. These two solubility values are shown on the diagram as large black points and are seen to agree excellently with the results obtained by the synthetic method. Kruyt's value of 2·2% at 169—170° for a mixture heated for a short time agrees well enough with our result; we are, however, unable to confirm the increase in solubility which he found when the heating was prolonged. Furthermore, we find by both the synthetic and the analytic method that the solubility of benzoic acid in sulphur decreases from 169° to 183° (2·30% to 2·04%), whereas Kruyt finds 5·8% at 185° (*loc. cit.*, p. 333).

The discrepancy is probably due to the fact that Kruyt's mixtures were heated in contact with the air, whereas ours were enclosed in sealed tubes. Liquid sulphur can readily be shown to undergo considerable oxidation in the air at the temperatures employed, and the presence of sulphur oxides in the sulphur layer would obviously account for the high values for solubilities deduced from the alkali titre of such a layer. In order to test this view, we heated a mixture in an unsealed tube at the temperature of boiling phenetole (169°) for 10 hours; on analysis the sulphur layer was found to have an apparent content of 2·62% of benzoic acid and gave a positive test for the presence of sulphuric acid with barium chloride.

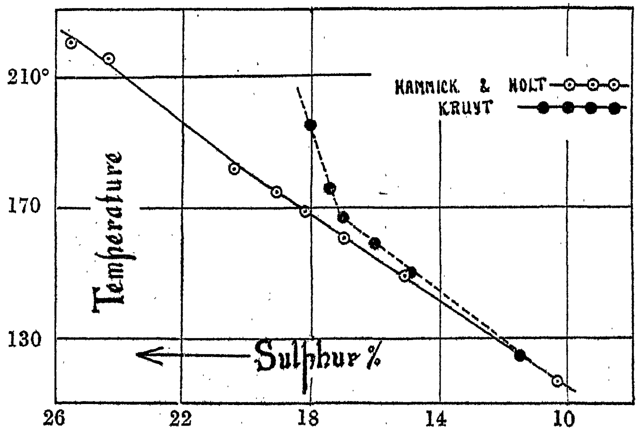
It thus seems to be established that on the sulphur side of the diagram the equilibrium curve is of Kruyt's Type η; our experiments, however, give no indication of a corresponding inflexion on the benzoic acid side. Our equilibrium temperatures and compositions are given in Table II and are plotted, together with Kruyt's data, in Fig. 2. It will be seen that again we do not agree with Kruyt, whose figures indicate a break in the curve at about 170°.

TABLE II.

Sulphur (%)	10·35	15·1	16·9	18·2	19·25	20·4	24·3	25·5
Temp.	117°	149·5°	160·5°	168·5°	175°	182°	215°	220°

These equilibria were determined as described above for the sulphur side of the system. The temperatures at which the clouds of second liquid phase separated on slow cooling were sharp, reproducible to within 1°, and remained unchanged on keeping the bulbs for several days. Owing, however, to the rapidity with which the droplets coagulated into large drops, it was not possible to obtain equilibrium temperatures by noticing temperatures at which the droplets disappeared.

FIG. 2.



The benzoic acid side of the system thus appears to be simple. The absence of the clouding and clearing phenomena found on the other side makes it practically certain that the minute region of retrograde solubility found there has no counterpart on the benzoic acid side.

Summary and Conclusion.

The diagrammatic representation of the equilibria in the system sulphur–benzoic acid is, on the sulphur side, of Kruyt's Type η. On the benzoic acid side, it is of the type ordinarily found for two partly miscible liquids. The facts embodied in the whole phase-diagram give an adequate explanation of the clouding phenomena noticed by Kruyt, without the necessity for his conclusion that in the neighbourhood of 170° three liquid layers can coexist.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, January 3rd*, 1927.]

LXXIII.—*The Effect of Pressure on the Limits for the Propagation of Flame in Ether–Air.*

By ALBERT GREVILLE WHITE.

IN a sufficiently large vessel a wide range of ether–air mixtures can propagate flame upwards or horizontally. Each of these ranges actually consists of two overlapping ranges which differ considerably in character and can be separated under appropriate conditions. Thus the addition of the requisite quantity of acetone to ether–air can give mixtures having two ranges that propagate flame separated by a range that will not (White, J., 1922, **121**, 2561). A similar pair of ranges is given by ether–air alone for horizontal propagation in a narrow tube (2·5 cm. diam.), and within each range the speed of flame increases to a maximum and then decreases as the ether concentration of the mixture is increased (*idem, ibid.*, p. 1244).

FIG. 1.

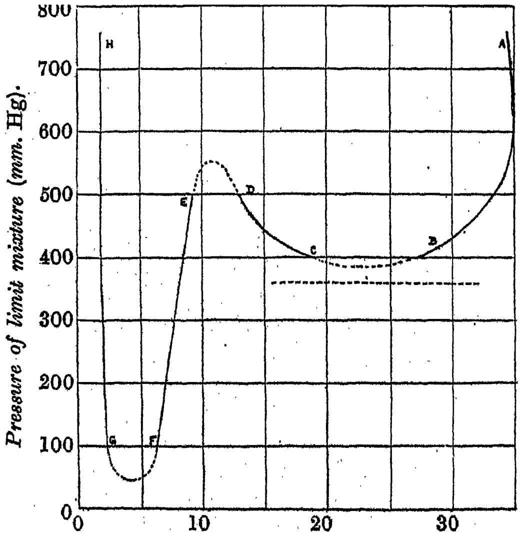


Figure showing the ranges of ether–air mixtures that can propagate flame horizontally at various pressures.

The results of an examination of the effect of pressure on the limits for the horizontal propagation of flame in ether–air are shown graphically in Fig. 1, and clearly demonstrate the existence of two entirely different propagation ranges. They also provide an explanation of results obtained during similar experiments by

White and Price (J., 1919, **115**, 1462), when the means of ignition adopted was such that the cool-flame range could normally only be obtained as an extension of the ordinary range.

The first notable effect of reduction of pressure is the separation into two ranges, of which the one containing more ether, the cool-flame range ABCD, diminishes rapidly and disappears entirely before the pressure has been reduced to 360 mm. The lower limit changes little until the pressure is 300 mm., but the upper limit of the "ordinary" range EFGH decreases fairly uniformly from 500 mm. to 90 mm. pressure.

EXPERIMENTAL.

The limits were all determined in cylindrical glass tubes 1·5 m. long and 5·1 cm. in diameter, but their *absolute* values would certainly be altered somewhat by any serious change in the diameter of the tube. The mixture for test was made up in the limit tube by introducing a weighed quantity of ether into the evacuated tube. All mixtures were made up and mixed at the ordinary pressure, and brought to the required pressure just before trial by means of a Gaede box pump. Ignition was effected by either a spark from a Sanax 20-inch coil or an electrically heated helix of platinum wire. The former was more suitable for the production of ordinary flames, and the latter for cool flames. Care had to be taken to use the appropriate means of ignition in any particular case. The flames given within the range ABCD were all of the cool variety and had to be observed in a darkened room. The cool-flame results were determined only to the nearest whole number. The results were all determined at 14—19°, and are given as percentages by volume.

Original pressure of ether–air mixture (mm. Hg).	Ranges of ether–air that would propagate flame horizontally.	
758	1·88—34	
660	—35	
590	1·87—35	
500	1·88— 9·25	and 13—33
440	—	and 15—31
400	1·88— 8·4	and 19—27
360	1·89— 8·1	No cool flame detected.
300	— 7·5	
240	1·98—	
190	2·05— 6·9	
90	2·32— 6·1	

I desire to thank Messrs. Nobel Industries, Ltd., and particularly Mr. W. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

THE NOBEL LABORATORIES, ARDEER. [*Received, December 4th*, 1926.]

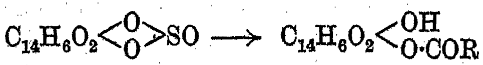
LXXIV.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part I. Thionylpyrocatechol and Dichlorothionylquinol.*

By ALBERT GREEN.

THIS paper is the first of a series in which it is proposed to deal primarily with the thionyl and the chlorothionyl compounds of hydroxybenzenes and, in particular, to study quantitatively their decomposition by weak organic acids, with a view to apply the information obtained to the more complex anthraquinone derivatives (J., 1924, **125**, 1450; 1926, 2198).

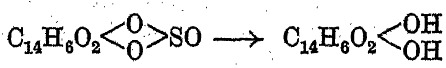
In the anthraquinone series two types of decomposition have been observed: one, which will be termed the *acyl decomposition*, is undergone by thionylalizarin, which is quantitatively converted by such acids into the 2-acyl derivative (I); the other type, the *hydroxylic decomposition*, is exemplified by thionylhystazarin, which reverts entirely to the hydroxy-compound (II). 2 : 3-Thionylanthragallol represents an intermediate case and gives a mixture of anthragallol and a monoacyl derivative.

(I.)



$$C_{14}H_6O_2{<}\substack{O\\O}{>}SO \longrightarrow C_{14}H_6O_2{<}\substack{OH\\O\cdot COR}$$

(II.)



$$C_{14}H_6O_2{<}\substack{O\\O}{>}SO \longrightarrow C_{14}H_6O_2{<}\substack{OH\\OH}$$

Repetition of the method employed by Anschütz and Posth (*Ber.*, 1894, **27**, 2752) in the preparation of thionylpyrocatechol ("catechol sulphite") showed that the solid by-products mentioned by them form the greater part of the yield. A method of preparation resembling that used by Richter (*Ber.*, 1916, **49**, 2339) in the preparation of some thionyl derivatives of monohydric phenols was adopted.

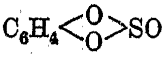
Thionylpyrocatechol is much more stable to moisture than thionylalizarin, but after exposure to the air for 6 days it reverts completely to the hydroxy-compound. It reacts very slowly with acetic acid or acetic anhydride, even when heated under pressure at 180°, but the addition of a trace of pyridine to the boiling acid solution results in its complete conversion into *monoacetylpyrocatechol.* This compound affords a means of obtaining mixed diacyl derivatives, one of which, *acetylbenzoylpyrocatechol*, is described. With acetic anhydride and a little pyridine, thionylpyrocatechol gives diacetylpyrocatechol in quantitative yield.

Attempts to prepare a chlorothionyl derivative of quinol in the presence of solvents gave stable, complex products which were analysed but not further investigated. Eventually *dichlorothionylquinol* was obtained as extremely unstable, white crystals which could be preserved only under thionyl chloride; when kept in sealed tubes for 2 days, they liquefied and considerable pressure was developed. In the air the dichlorothionyl compound fumed copiously and was rapidly converted into quinol; with boiling acetic acid or acetic anhydride it formed diacetylquinol in theoretical yield. *p*-Benzoquinone was recognised among the products of its complex auto-decomposition.

The acyl decomposition of dichlorothionylquinol was unexpected, since, in the conversion of 1 : 2-thionyl-7-chlorothionylanthrapurpurin (*loc. cit.*, p. 2198) into a monoacetylanthrapurpurin by acetic acid, the evidence points to the replacement of the chlorothionyl group by hydrogen.

Attempts to prepare thionyl and chlorothionyl derivatives of resorcinol yielded stable, high melting, insoluble products which analyses showed to be very complex. Richter (*loc. cit.*, p. 2345) states that he obtained the " sulphites " of several phenols including resorcinol, but he gives neither descriptions of the compounds nor analytical data. The author has carried out many preparations under various conditions, and has carefully repeated Richter's method several times, without obtaining such a compound. If indeed a simple derivative is obtainable, resorcinol would be expected to give a dichlorothionyl rather than a thionyl compound.

EXPERIMENTAL.

Thionylpyrocatechol,  $C_6H_4{<}^{O}_{O}{>}SO$.—To a cooled solution (10°) of 30 g. (1 mol.) of pyrocatechol in 150 c.c. of dry carbon disulphide and 43·0 c.c. (2 mols.) of pyridine, were added, with continuous stirring, 20·3 c.c. (1 mol.) of freshly-distilled thionyl chloride in 80 c.c. of dry carbon disulphide. After standing at 10° for 30 minutes, the mixture was boiled on the water-bath for a similar time. While still warm, the faintly yellow carbon disulphide solution was decanted from the syrupy layer of pyridine hydrochloride, which was washed several times with small quantities of the warm solvent. The carbon disulphide solution and washings were concentrated on the water-bath, and the last traces of the solvent were removed in a vacuum over paraffin wax. Thionylpyrocatechol (41 g.) was thus obtained as a faintly yellow, mobile liquid, b. p. 137—138°/105 mm. (Found: S, iodometrically as sulphur dioxide in the solution in aqueous sodium hydroxide, 20·3, 20·4. Calc.: S, 20·5%).

Decomposition with acetic acid. (A) A solution of thionylpyrocatechol in acetic acid, after boiling for 12 hours, still contained unchanged sulphite. This was shown by stirring the solution into water and washing the insoluble portion thoroughly; the alkaline solution of this decolorised acidified iodine solution.

(B) *Monoacetylpyrocatechol*, OH·C_6H_4·OAc. A solution of 16 g. of thionylpyrocatechol in 40 c.c. of glacial acetic acid and 3 drops of pyridine was boiled for 6 hours; evolution of sulphur dioxide was then no longer appreciable. The *monoacetyl* derivative was obtained by fractional distillation as a colourless, viscous liquid (14 g.), b. p. 189—191°/102 mm. In a freezing mixture, it set to a felted mass of thin, white plates, which, after draining on a porous tile, melted at 57—58°, were soluble in cold water, and gave a bottle-green colour with ferric chloride (Found: C, 63·0; H, 5·3; CH_3·CO, 28·0. $C_8H_8O_3$ requires C, 63·2; H, 5·3; CH_3·CO, 28·3%).

Acetylbenzoylpyrocatechol, OAc·C_6H_4·OBz. A solution of 7·0 g. (1 mol.) of monoacetylpyrocatechol in 10 c.c. of pyridine was treated with 5·5 c.c. (1 mol.) of benzoyl chloride, and after warming slightly, was stirred into cold dilute hydrochloric acid. The oily precipitate was separated, washed thoroughly with cold water, and taken up in ether. *Acetylbenzoylpyrocatechol* was obtained from the dried ethereal solution as a thick syrup (11 g.) which slowly solidified in fine, white needles, m. p. 78°. After recrystallisation from light petroleum–acetone it showed the same melting point (Found: C, 70·1; H, 4·7; CH_3·CO, 16·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7; CH_3·CO, 16·8%). The substance is easily soluble in the cold in the common organic solvents except light petroleum, insoluble in water, and its alcoholic solution gives no colour with ferric chloride.

Diacetylpyrocatechol. Thionylpyrocatechol (5. g.) in acetic anhydride (15 c.c.) containing one drop of pyridine was boiled until sulphur dioxide was no longer evolved (40 minutes). The solution, when stirred into cold water, gave a white solid (6·5 g.), which crystallised from rectified spirits in short, white rods melting at 64° alone and when mixed with pure diacetylpyrocatechol (Found: CH_3·CO, 44·3. Calc.: CH_3·CO, 44·3%).

Dichlorothionylquinol, $C_6H_4(O{\cdot}SOCl)_2$.—Ice-cold thionyl chloride (200 c.c.) was added slowly to a mixture of quinol (40 g.) and pyridine (3 drops) contained in a flask fitted with a ground-in reflux condenser. Reaction commenced in the cold with evolution of hydrogen chloride, and was allowed to proceed at 15° for 2 hours; a dark orange-coloured solution had then been formed. This was boiled on the water-bath for 3 hours, concentrated to about 120 c.c., and kept dry.

The small, white crystals (about 30 g.) which separated were filtered off as required, and rapidly washed with dry benzene and absolute ether. They melted at 75° to a pale orange liquid (Found: C, 26·6, 26·4; H, 1·6, 1·7; * S, 23·2, 23·3; Cl, 25·7, 25·7. $C_6H_4O_4Cl_2S_2$ requires C, 26·2; H, 1·5; S, 23·3; Cl, 25·8%). By decomposition by the moisture of the air, followed by drying in a vacuum over sulphuric acid, 3·0026 g. of dichlorothionylquinol gave 1·1990 g. of quinol (theory requires 1·2010 g.), and 1·1240 g. yielded 0·4482 g. (theory requires 0·4496 g.). These products melted at 169° either alone or when mixed with pure quinol.

Dichlorothionylquinol fumes copiously in the air, and becomes yellow within one minute. It reacts violently with water and with aqueous and alcoholic solutions of potassium hydroxide. Even when stored in a dry atmosphere at room temperature, it decomposed to a complex mixture in which free sulphur was recognised.

Thermal decomposition. Dichlorothionylquinol was heated gradually from 70° to 150°. Decomposition commenced at about 95°. The sublimates were collected and yielded the characteristic yellow needles of *p*-benzoquinone, which was recognised by its odour and m. p. (116°, either alone or mixed with an authentic specimen). A small quantity of white, feathery crystals, m. p. 135°, which sublimed at a higher temperature than the quinone were not obtained in sufficient amount for analysis. The residue in the tube yielded no recognisable substance.

Decomposition with acetic acid. A solution of 4·0 g. of dichlorothionylquinol in 10 c.c. of glacial acetic acid was boiled for 15 minutes; hydrogen chloride and sulphur dioxide were then no longer perceptible at the mouth of the flask. When cold, the solution deposited 1·8 g. of lustrous, white plates of diacetylquinol (0·8 g. also was obtained by stirring the filtrate into water), m. p. 122°, alone and when mixed with the pure substance (Found: $CH_3{\cdot}CO$, 44·4. Calc.: $CH_3{\cdot}CO$, 44·3%).

Decomposition with acetic anhydride. The red solution of 2 g. of the dichlorothionyl compound in 5 c.c. of acetic anhydride, when boiled rapidly, became pale orange and evolved hydrogen chloride and sulphur dioxide very vigorously. After 8 minutes, the solution was cooled, and deposited white plates (0·8 g.) of diacetylquinol which, alone or mixed with an authentic specimen, melted at 123° (Found: $CH_3{\cdot}CO$, 44·1. Calc.: $CH_3{\cdot}CO$, 44·3%).

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* Owing to the unstable nature of the compound, better analyses for carbon and hydrogen were not obtained, although both lead chromate and silver gauze were used in the combustion tubes. Satisfactory results for sulphur and chlorine were given by the Carius method.

A portion of the expenses of this research has been defrayed by a grant from the Research Fund Committee of the Chemical Society, to whom the author wishes to express his thanks.

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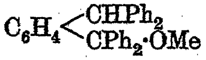
ABERYSTWYTH. [*Received, December 20th,* 1926.]

LXXV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part I.*

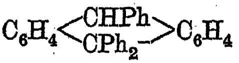
By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and IVOR GRAY NIXON.

THE interest which attaches to the three-carbon transannular tautomerism exhibited by certain *meso*-alkyl anthracenes (Barnett, Cook, Matthews, *Ber.*, 1926, **59**, 1429, 2863) has rendered it desirable to review the methods available for the preparation of these compounds. Such methods fall roughly into two classes according as the *meso*-substituent is attached prior or subsequent to the closing of the central ring of the anthracene complex. The present communication deals with the former class of reaction.

(*A*). By treating methyl triphenylmethane-*o*-carboxylate with magnesium phenyl bromide, Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 979) obtained a product which, when treated with hydrogen chloride in glacial acetic acid, passed into 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene (II).

(I.) 

$$C_6H_4<\begin{matrix}CHPh_2\\CPh_2\cdot OMe\end{matrix}$$

 (II.

$$C_6H_4<\begin{matrix}CHPh\\CPh_2-\end{matrix}>C_6H_4$$

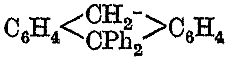
They described their product as a methyl ether (I), but offered no evidence of the presence of the methoxyl group other than ultimate analysis, which in this case is totally insufficient to differentiate between the free hydroxy-compound and its methyl ether (Found: C, 89·7; H, 6·2. $C_{32}H_{26}O$ requires C, 90·1; H, 6·1. $C_{33}H_{28}O$ requires C, 90·0; H, 6·4%), and it has now been found that the compound is, as would be expected, the free hydroxy-compound, since identical products are obtained from the methyl and the ethyl ester.

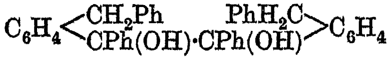
With diphenylmethane-*o*-carboxylic acid (*o*-benzylbenzoic acid), which is easily accessible, a synthesis similar to the above might be expected to take place. To a limited extent this is true, as the esters of this acid, on treatment with magnesium phenyl bromide, yield an oily product (undoubtedly III) which is easily and almost quantitatively dehydrated to 9 : 9-diphenyl-9 : 10-dihydroanthracene (IV). Attempts to extend this synthesis by replacing the magnesium phenyl bromide by magnesium ethyl, *iso*propyl or naphthyl bromide or by magnesium benzyl chloride were not successful, as no crystalline substance could be obtained from the viscid products of the reaction.

The hydroxy-compound (III) is not the sole product of the action of magnesium phenyl bromide on the esters of *o*-benzylbenzoic acid, a second product being formed at the same time to which formula (V) is given, this formula being based on analysis and molecular-weight determinations, the oxidation of the substance to *o*-dibenzoylbenzene, and on the fact that its formation is independent of the alcoholic radical (methyl, ethyl, or phenyl) in the ester.

(III.)

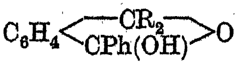
$C_6H_4<\!\begin{array}{l}CH_2Ph\\CPh_2{\cdot}OH\end{array}$


$C_6H_4<\!\begin{array}{l}CH_2\text{-}\\CPh_2\end{array}\!>C_6H_4$
(IV.)

(V.)

$C_6H_4<\!\begin{array}{l}CH_2Ph\qquad\quad PhH_2C\\CPh(OH){\cdot}CPh(OH)\end{array}\!>C_6H_4$

This pinacol obviously originates by the reduction of the ketone (*o*-benzylbenzophenone) which must be the first product of the action of magnesium phenyl bromide on the esters of *o*-benzylbenzoic acid, and, although the reducing action of Grignard solutions is well known, this appears to be the first case recorded in which they have been found to cause pinacol condensation.

(*B*). By treating diphenylphthalide with magnesium phenyl bromide, Guyot and Catel (*Bull. Soc. chim.*, 1906, **35**, 551, 562) obtained a compound which they described as a hydroxyphthalan (VI, R = Ph), tetraphenylphthalan (VIII) being obtained by employing a large excess of the Grignard solution (Schlenk and Brauns, *Ber.*, 1915, **48**, 727).


$C_6H_4<\!\begin{array}{l}CR_2\\CPh(OH)\end{array}\!>O$
(VI.)

$C_6H_4<\!\begin{array}{l}CR_2{\cdot}OH\\COPh\end{array}$
(VII.)

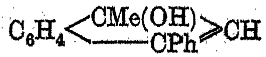
$C_6H_4<\!\begin{array}{l}CPh_2\\CPh_2\end{array}\!>O$
(VIII.)

Guyot and Catel's compound cannot be dehydrated to give diphenylanthrone by treatment either with hydrogen chloride in glacial acetic acid or with concentrated sulphuric acid, but it does give diphenylanthrone on heating to 300°.

Similar compounds (R = Me or Et) are obtained by the action of magnesium phenyl bromide on dimethyl- and diethyl-phthalide; these, however, on heating do not pass into the corresponding dialkylanthrones, but lose water in a different direction to give unsaturated substances which are probably represented by formulæ (IX) and (X), although the possibility that they may be indene derivatives (*e.g.*, XI) is not excluded.

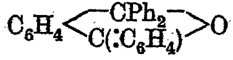
$C_6H_4<\!\begin{array}{l}CMe{:}CH_2\\COPh\end{array}$
(IX.)

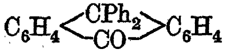
$C_6H_4<\!\begin{array}{l}CEt{:}CHMe\\COPh\end{array}$
(X.)


$C_6H_4<\!\begin{array}{l}CMe(OH)\\CPh\end{array}\!>CH$
(XI.)

No proof of the hydroxyphthalan structure (VI) is at present available, and the hydroxy-ketonic structure (VII) is suggested by Beilstein ("Handbuch," 4th Ed., Vol. VIII, p. 223). It is possible that the two formulæ may represent phases of an isodynamic change and it is proposed to investigate this point at a later date and at the same time to examine the dehydration products more closely. In the meantime the hydroxyphthalan structure is retained in the following, although the dehydration which takes place on heating is better explained by formula (VII).

(*C*). Arylhydroxyphthalans (VI or VII) have been obtained from the esters of phthalic acid by Guyot and Catel (*loc. cit.*) and by Weiss and Heidrich (*Monatsh.*, 1924, **45**, 210). Shibata (J., 1909, **95**, 1449) treated diethyl phthalate with magnesium phenyl bromide and after purifying his product by distillation under reduced pressure (b. p. 280—295°/8 mm.) isolated a colourless, crystalline substance which he described as diphenylphenylenephthalan (XII), and he based certain conclusions concerning the structure of the benzene ring on its formation. The formula given by Shibata appeared in the highest degree improbable and repetition of his experiments has proved that this supposed phenylene compound is really diphenylanthrone (XIII), the formation of which is undoubtedly due to dehydration of the hydroxyphthalan (VI or VII) first formed.

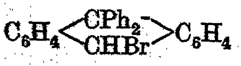
(XII.) 
$C_6H_4{<}\begin{matrix}CPh_2\\C(:C_6H_4)\end{matrix}{>}O$

 (XIII.)
$C_6H_4{<}\begin{matrix}CPh_2\\CO\end{matrix}{>}C_6H_4$

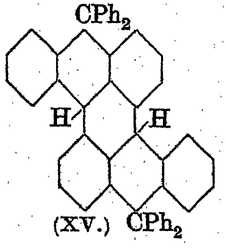
Shibata's conclusions as regards the structure of the benzene ring are therefore valueless.

The action of magnesium phenyl bromide on *o*-dibenzoylbenzene also leads to the hydroxyphthalan (VI or VII) and from this to diphenylanthrone.

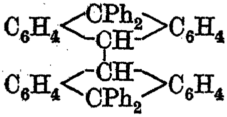
(*D*). Liebermann and Lindebaum (*Ber.*, 1905, **38**, 1804), by heating 9-bromo-10 : 10-diphenyl-9 : 10-dihydroanthracene (XIV) alone or with naphthalene, obtained a product which they described as tetraphenylheptacyclene and to which they gave formula (XV), without, however, bringing forward any experimental evidence in


$C_6H_4{<}\begin{matrix}CPh_2\\CHBr\end{matrix}{>}C_6H_4$

(XIV.)



(XV.)

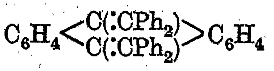

$$\begin{matrix}C_6H_4{<}\begin{matrix}CPh_2\\CH\end{matrix}{>}C_6H_4\\ |\\ C_6H_4{<}\begin{matrix}CH\\CPh_2\end{matrix}{>}C_6H_4\end{matrix}$$

(XVI.)

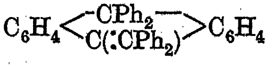
its favour. The formation of a compound of this structure by the above reaction is not very probable, and an exactly similar, insoluble and highly stable substance is formed when diphenylanthrone is submitted to the pinacol reduction with zinc and hydrochloric acid in acetic acid solution, and also when 9 : 9-diphenyl-9 : 10-dihydroanthracene is heated to 250° in oxygen or is heated with benzal chloride or benzophenone chloride. Owing to the extreme insolubility of these substances and to the fact that they do not melt, it is impossible to state with certainty that they are identical, but it seems extremely probable that they are identical with the so-called tetraphenylheptacyclene and have formula (XVI). The impossibility of purifying them by recrystallisation renders it difficult to be certain that the molecule does not contain two hydrogen atoms less than the number required by the formula given ($C_{52}H_{38}$ requires C, 94·3; H, 5·7. $C_{52}H_{36}$ requires C, 94·6; H, 5·45%).

(*E*). Padova (*Ann. Chim.*, 1910, **19**, 400) found that dihydroanthracene condensed with benzophenone chloride to give bisdiphenylmethylenedihydroanthracene (XVII), the compound obtained by Staudinger (*Ber.*, 1908, **41**, 1362) by the action of diphenylketen on anthraquinone. 9 : 9-Diphenyldihydroanthracene behaves in the same way with benzophenone chloride and gives 9 : 9-diphenyl-10 : 10-diphenylmethylene-9 : 10-dihydroanthracene (XVIII), in which it has not been found possible to reduce the double bond.

(XVII.)



$$C_6H_4{<}\begin{matrix}C(:CPh_2)\\C(:CPh_2)\end{matrix}{>}C_6H_4$$



$$C_6H_4{<}\begin{matrix}CPh_2\text{---}\\C(:CPh_2)\end{matrix}{>}C_6H_4$$

(XVIII.)

Padova (*loc. cit.*) claimed to have reduced his compound by means of sodium and boiling benzyl alcohol, but we have not been able to repeat this.

EXPERIMENTAL.

ωω-*Diphenyl*-o-*tolyldiphenylcarbinol.*—The methyl and *ethyl* esters of triphenylmethane-*o*-carboxylic acid were prepared in the usual way by esterification with the alcohol and hydrochloric acid. The former (m. p. 98°) has been prepared by Haller and Guyot (*loc. cit.*), by a different method. The latter, after being twice recrystallised from alcohol, formed a colourless, crystalline powder, m. p. 69° (Found: C, 83·2; H, 6·6. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%).

In each case, an ethereal solution of the ester was added to an ethereal solution of magnesium phenyl bromide (2 mols.) with cooling in a freezing mixture, and the whole was boiled for 4 hours and then poured on to a mixture of ice and solid ammonium chloride. The solid which separated and that which was obtained by distilling off the ether from the ethereal solution were identical and in each case, after recrystallisation from toluene–light petroleum, melted at 218°, and a mixture of the specimens made from each ester showed no depression of melting point.

o-*Benzylbenzoic Acid.*—The statement by Ullmann (*Annalen*, 1896, **291**, 23) that *o*-benzoylbenzoic acid cannot be reduced beyond the phthalide stage by means of ammonia and zinc dust is incorrect, the following method having been found to be the most convenient one for the preparation of *o*-benzylbenzoic acid. Technical *o*-benzoylbenzoic acid (150 g.) was dissolved in 1 l. of concentrated ammonia (*d* 0·880) diluted with 300 c.c. of water, and a few c.c. of copper sulphate solution were added, followed by 300 g. of zinc dust in several portions with cooling. The whole was heated on the water-bath until a filtered sample, when acidified, gave a precipitate which was completely soluble in sodium carbonate (about 2 days). The filtrate and washings were then acidified with hydrochloric acid, and the precipitate was dissolved in sodium carbonate solution, reprecipitated with hydrochloric acid, and finally recrystallised from aqueous acetic acid. The yield was 117 g. of snow-white material, m. p. 118°.

Gresley (*Annalen*, 1886, **234**, 234) states that *o*-benzylbenzoic acid on treatment with sulphuric acid does not give anthrone but is oxidised to anthraquinone. This is erroneous, for when a solution of benzylbenzoic acid in concentrated sulphuric acid is kept for 2 hours at the ordinary temperature an almost quantitative yield of anthrone is obtained, and indeed this is a convenient method of preparing anthrone.

The *methyl* and *ethyl* esters were prepared in the usual way by means of the alcohol and hydrochloric acid and formed oils, b. p. 320° and 325°, respectively. The *phenyl* ester was obtained from the acid, phenol, and thionyl chloride in pyridine solution (Barnett and Nixon, *Chem. News*, 1924, **129**, 190) and was used in the crude state.

9 : 9-*Diphenyl*-9 : 10-*dihydroanthracene* (IV).—To an ethereal solution of magnesium phenyl bromide prepared from 8 g. of magnesium and 48 g. of bromobenzene and cooled in a freezing mixture, an ethereal solution of 32 g. of ethyl *o*-benzylbenzoate was added slowly. After boiling for an hour, or being kept at the ordinary temperature over-night, the whole was poured into ice and dilute hydrochloric acid, and the solid (15 g.; see below) collected. After washing and drying, the ether was removed from the ethereal solution. The viscid residue, which refused to crystallise, was heated for an hour on the water-bath with a glacial acetic acid solution of hydrogen chloride. The resulting diphenyldihydroanthracene (18 g.), m. p. 200°, was quantitatively oxidised to diphenylanthrone by chromic acid in glacial acetic acid.

Similar results were obtained when the methyl and the phenyl ester were used in place of the ethyl ester.

s-oo′-*Dibenzylbenzpinacol* (V).—The solid by-product insoluble in ether obtained as described above, after recrystallisation from benzene–light petroleum, chloroform–light petroleum, and methyl ethyl ketone, formed a colourless, crystalline powder, m. p. 175°. Its hot benzene solution showed a strong green fluorescence which vanished on cooling (Found: C, 87·8; H, 6·5; *M*, in ethylene dibromide, 540. $C_{40}H_{34}O_2$ requires C, 87·9; H, 6·2%; *M*, 546).

When 1 g. of the above pinacol in 20 c.c. of boiling glacial acetic acid was treated slowly with a concentrated aqueous solution of 3 g. of chromic acid, oxidation took place rapidly and, on cooling and dilution, a solid was obtained which, after recrystallisation, was identified as *o*-dibenzoylbenzene by direct comparison with an authentic sample.

Attempts to convert the pinacol into a dianthranyl derivative, an acetate, and a benzoate gave oily products only. The pinacol was not regenerated from these oils on boiling with alcoholic alkali, but they were converted into *o*-dibenzoylbenzene by oxidation with chromic acid. It is therefore likely that loss of water with formation of an α-pinacolin had taken place, but owing to the uninviting nature of the products the matter was not further investigated.

Dimethylphenylhydroxyphthalan (VI or VII; R = Me).—An ethereal solution of 8 g. of dimethylphthalide was added with water-cooling to an ethereal solution of magnesium phenyl bromide prepared from 2 g. of magnesium and 12 g. of bromobenzene. After boiling for 2 hours, the whole was poured on to ice and hydrochloric acid, and the ethereal layer was washed with sodium hydroxide solution and with water, dried over sodium sulphate, concentrated, and diluted with light petroleum. The m. p., 118°, of the resulting crystals (9·7 g.) was not altered by further recrystallisation from benzene–light petroleum (Found: C, 80·0; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

o-iso*Propenylbenzophenone* (IX).—On distillation at atmospheric pressure, the above phthalan (10 g.) gave water and a product, b. p. 305°, which was dried in ethereal solution and distilled under reduced pressure; the yellow oil, b. p. 208—209°/45 mm., obtained became solid on cooling and after recrystallisation from aqueous alcohol formed colourless needles, m. p. 44° (Found: C, 86·2; H, 6·4. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%).

*o-iso*Propenylbenzophenone at once decolorised a solution of bromine in carbon tetrachloride. After 1 g. in 15 c.c. of glacial acetic acid had been boiled for an hour with addition of a concentrated aqueous solution of 5 g. of chromic acid, a solid was obtained, on cooling and dilution, which was reprecipitated from its solution in aqueous sodium carbonate and then identified as *o*-benzoylbenzoic acid by direct comparison with an authentic sample.

Diethylphenylhydroxyphthalan (VI or VII; R = Et) was prepared from diethylphthalide and magnesium phenyl bromide in exactly the same way as the corresponding dimethyl derivative described above and formed colourless, glistening crystals, m. p. 94—95° (Found: C, 80·2; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·5; H, 7·5%). On heating, it lost water and passed into an unsaturated oil which was not further examined.

Attempts to prepare the dibenzyl analogue from dibenzylphthalide were not successful, most of the dibenzylphthalide being recovered unchanged.

Action of Magnesium Phenyl Bromide on Ethyl Phthalate.—The experiment was carried out essentially as described by Shibata (*loc. cit.*), and the product identified as diphenylanthrone by direct comparison with an authentic sample.

Action of Magnesium Phenyl Bromide on o-*Dibenzoylbenzene.*—Finely powdered *o*-dibenzoylbenzene (14·5 g.) was added with cooling to an ethereal solution of magnesium phenyl bromide prepared from 1·25 g. of magnesium and 8 g. of bromobenzene. After boiling for 6 hours, the whole was poured into ice and dilute sulphuric acid, unchanged *o*-dibenzoylbenzene (2·5 g.) removed by filtration, and the ether distilled off. The residue, after purification by distillation in steam and drying in ethereal solution, was heated at 300° for ½ hour, and after recrystallisation was identified as diphenylanthrone by direct comparison with an authentic sample.

In both the above preparations of diphenylanthrone it is probable that triphenylhydroxyphthalan (VI or VII; R = Ph) intervenes, as it was found that this substance passed into diphenylanthrone when heated at 300° for ½ hour. Dehydration to diphenylanthrone, however, could not be effected either with concentrated sulphuric acid or with hydrogen chloride in acetic acid.

Tetraphenyltetrahydrodianthranyl (XVI).—(*a*) Diphenylanthrone (4·4 g.) and 2·5 g. of zinc dust were boiled with 50 c.c. of glacial acetic acid, and 5 c.c. of fuming hydrochloric acid were added slowly. After 5 hours, the solid was collected, extracted with hydrochloric acid and with boiling glacial acetic acid, and then recrystallised from a very large volume of boiling nitrobenzene, in which, however, it was almost insoluble. The resulting cream-coloured powder did not melt at 320° (Found: C, 93·9; H, 5·75. $C_{52}H_{38}$ requires C, 94·3; H, 5·7%).

(*b*) Diphenyldihydroanthracene was heated for 2 hours in a current of oxygen at 250°, and the product repeatedly extracted with boiling xylene to remove impurities. After being washed with ether and dried, it formed a colourless, crystalline powder which did not melt at 340° (Found : C, 94·3 ; H, 5·9%).

(*c*) An insoluble product similar to the above was obtained when diphenyldihydroanthracene was heated at 250° with benzal chloride.

9 : 9-*Diphenyl*-10 : 10-*diphenylmethylene*-9 : 10-*dihydroanthracene* (XVIII).—9 : 9-Diphenyl-9 : 10-dihydroanthracene (6·6 g.) and benzophenone chloride (5 g.) were heated for 2 hours at 250°, and coloured resinous by-products removed by washing with ether. The residual solid (7·8 g.) was dissolved in boiling xylene, and a small amount of an insoluble substance (probably tetraphenyltetrahydrodianthranyl) removed by filtration. On cooling, a colourless, crystalline powder separated which, after further recrystallisation, melted at 286° (Found : C, 94·0 ; H, 5·8. $C_{39}H_{28}$ requires C, 94·4 ; H, 5·6%).

The above compound was recovered unchanged after attempts to reduce it with zinc and hydrochloric acid in boiling glacial acetic acid, with sodium in boiling amyl and benzyl alcohols, and with hydriodic acid and red phosphorus at 180° for 7 hours.

10-*Chloro*-9 : 9 : 10-*triphenyl*-9 : 10-*dihydroanthracene*.—Five g. of triphenyldihydroanthranol (m. p. 204°, prepared from diphenylanthrone and magnesium phenyl bromide as described by Haller and Guyot, *Compt. rend.*, 1904, **139**, 9, but without the use of benzene as a solvent) were dissolved in 25 c.c. of benzene, and dry hydrogen chloride passed through the boiling solution for 20 minutes. On cooling and addition of ether, a solid was obtained which, after recrystallisation from benzene–ether, formed a colourless powder, m. p. 193—194°. It contained solvent of crystallisation which it lost at 120° (Found : Cl, 8·0. $C_{32}H_{23}Cl$ requires Cl, 8·0%). This chloro-compound, when boiled in benzene solution with copper powder in an atmosphere of carbon dioxide, gave a yellow solution which became more deeply coloured on heating. This solution probably contained a free radical, but further investigation has been postponed pending the publication of the work of another investigator.

9 : 9 : 10-*Triphenyl*-9 : 10-*dihydroanthracene* (II).—The preparation of this compound by the reduction of triphenyldihydroanthranol with zinc dust and acetic acid as described in the literature gave poor results, and it was found much better to reduce 15 g. of triphenyldihydroanthranol in 150 c.c. of boiling amyl alcohol by the addition of 7·5 g. of sodium. The solid which separated when the hot liquid was poured into water was washed with alcohol

and, after recrystallisation from benzene–alcohol (yield, 12 g.), melted at 230° (the m. p. given in the literature is 220°).

9 : 10-*Diphenyl*-9 : 10-*dihydroanthracene* was obtained most conveniently by reducing 1 g. of 9 : 10-diphenylanthracene in 25 c.c. of boiling amyl alcohol by the addition of 1 g. of sodium. The solution at first became yellow, but the yellow colour subsequently vanished with the fluorescence. The mixture was poured into water, the amyl alcohol removed with steam, and the product recrystallised from benzene–light petroleum.

Action of Aluminium Chloride on 9 : 9-*Diphenyl*-9 : 10-*dihydroanthracene*.—Diphenyldihydroanthracene (5 g.) and aluminium chloride (10 g.) were boiled for 6 hours with 50 c.c. of carbon disulphide. After decomposition with dilute hydrochloric acid, the carbon disulphide solution was washed with water, the solvent removed by distillation, and the product recrystallised from acetic acid and from alcohol. It then melted at 155—157°, alone or when mixed with an authentic sample of 9-phenylanthracene.

By the action of aluminium chloride on 9 : 10-diphenyl-9 : 10-dihydroanthracene, a product was obtained, m. p. 215—220°, which appeared to consist chiefly of 9 : 10-diphenylanthracene, since it did not depress the melting point of this substance; repeated recrystallisation, however, failed to raise the melting point.

The action of aluminium chloride on 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene in the cold led only to the recovery of the unchanged material, although the fluorescence of the solution and the low melting point of the crude recovered material indicated that re-establishment of the " bridge " had taken place to a slight extent. When the experiment was carried out in boiling carbon disulphide solution, only resinous products were obtained.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this research.

SIR JOHN CASS TECHNICAL INSTITUTE,
JEWRY STREET, E.C.3.
[*Received, December 29th,* 1926.]

LXXVI.—*The Complex Chlorides of Tervalent Molybdenum.*

By WILLIAM RALPH BUCKNALL, SYDNEY RAYMOND CARTER, and WILLIAM WARDLAW.

BY the addition of the appropriate alkali chloride to electrolytically reduced solutions of tervalent molybdenum, Chilesotti (*Atti R. Accad. Lincei*, 1903, [v], **12**, ii, 67) isolated the salts K_3MoCl_6 and

R_2MoCl_5,H_2O, where R = NH_4, Rb, and Cs. These represent two types of compounds common among tervalent elements. The conditions under which one or other type of salt could be obtained with certainty were not apparent to this investigator, but a recent research by Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458), in which they prepared R_3MoCl_6 and R_2MoCl_5,H_2O, where R = NH_4, K, Rb, or Cs, indicates, as would be expected, that the principal factor is acid concentration. So far, only an examination of their general reactions has been attempted. In view of the fact that they can be considered as co-ordination compounds, $R_3[MoCl_6]$ and $R_2[MoCl_5,H_2O]$, in which molybdenum exhibits a co-ordination number of six, it seemed of interest to determine whether such a formulation was justified.

The results obtained from physico-chemical determinations confirmed the above formulations for the salts, and at the same time furnished information as to the stability of the complex anion and the varying changes which the compounds undergo in aqueous solution.

EXPERIMENTAL.

Tripotassium Molybdenum Hexachloride.—The method of preparation was that of Chilesotti (*loc. cit.*). 350 C.c. of a solution of molybdenum trioxide (35 g.) in 8*N*-hydrochloric acid were reduced to the tervalent condition, concentrated to 150 c.c. (33% $MoCl_3$) and saturated with hydrogen chloride. One-half to three-quarters of the theoretical amount of pure potassium chloride (30—40 g.) was added as a 10% solution in air-free water and the mixture concentrated at 70° under reduced pressure, until crystallisation commenced. The liquid was now filtered and the filtrate saturated with hydrogen chloride until cold, whereupon the double salt separated. The crystals were washed with concentrated hydrochloric acid, alcoholic hydrochloric acid, and finally with alcohol, and dried in a vacuum.

Analysis. The molybdenum was precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide. The chloride in the filtrate and washings was estimated as silver chloride. The potassium was weighed as potassium sulphate (Found: Mo, 22·5; Cl, 50·2; K, 27·3. K_3MoCl_6 requires Mo, 22·5; Cl, 49·9; K, 27·5%).

Dipotassium Molybdenum Pentachloride.—This salt was isolated by Foerster and Fricke (*loc. cit.*) who, however, gave neither analyses nor details of preparation. The following method gave a satisfactory yield. 100 C.c. of the red solution containing tervalent molybdenum, prepared by the electrolysis of molybdenum trioxide (10 g. MoO_3) in 100 c.c. of 8*N*-hydrochloric acid, were added to

25 c.c. of a solution of potassium chloride (1 g.) and the mixture was concentrated in an air-free flask at 60—70° under reduced pressure to a volume of about 20 c.c. Air-free, absolute alcohol was now admitted and a bright brick-red crystalline precipitate separated, which, after filtration and washing with alcohol, was dried in a vacuum (Found: Mo, 26·0; Cl, 47·8. K_2MoCl_5,H_2O requires Mo, 26·0; Cl, 48·0%). In attempting to isolate this compound from very dilute acid solutions, as suggested by Foerster and Fricke, an oxysalt was obtained (*q. v.*).

Triammonium Molybdenum Hexachloride.—Both Foerster and Fricke (*loc. cit.*) and Rosenheim and Li (*Ber.*, 1923, **56**, 2225) have prepared this salt, but in neither case were experimental details given. The formula assigned by Foerster and Fricke was $(NH_4)_3MoCl_6$, whilst the analyses of the other authors corresponded to $(NH_4)_3MoCl_6,2{\cdot}5H_2O$.

Preparation. 80 C.c. of the concentrated solution containing tervalent molybdenum (33% $MoCl_3$) were saturated with hydrogen chloride, added to a saturated aqueous solution of ammonium chloride (20 g.), and the mixture concentrated to the crystallising point. The diammonium molybdenum pentachloride thus formed was removed, and the filtrate again saturated with hydrogen chloride until cold. Small rose-coloured crystals separated which, after washing free from hydrochloric acid with aqueous alcohol, were dried in a vacuum.

Analysis. The molybdenum and chloride were estimated as above, and the ammonium by the distillation method. In this method, the ammoniacal distillate was titrated continuously against standard acid, using bromophenol-blue (0·04% solution) as indicator [Found: Mo, 25·2; Cl, 56·3; NH_4, 14·1. $(NH_4)_3MoCl_6,H_2O$ requires Mo, 25·2; Cl, 55·9; NH_4, 14·2%].

Diammonium Molybdenum Pentachloride.—This was prepared by the following method of Chilesotti: To 175 c.c. of the concentrated solution (33% $MoCl_3$) containing tervalent molybdenum, 25 g. of ammonium chloride as a 10% aqueous solution were added, and the mixture was concentrated at 70° under reduced pressure, until the salt crystallised as a bright brick-red compound [Found: Mo, 29·2; Cl, 54·4; NH_4, 11·0. $(NH_4)_2MoCl_5,H_2O$ requires Mo, 29·3; Cl, 54·2; NH_4, 11·0%].

Cæsium and Rubidium Salts.—These were prepared from solutions of the above salts by double decomposition with the alkali chlorides. They were also obtained by the addition of the corresponding alkali chlorides to the concentrated solution containing tervalent molybdenum and subsequent evaporation. Salts of the type R_3MoCl_6 were prepared in a similar manner from more concentrated acid solutions (Found: Mo, 21·0; Cl, 38·6. Rb_2MoCl_5,H_2O requires Mo, 20·8; Cl, 38·4%. For Cs_2MoCl_5,H_2O, found: Mo, 17·4; Cl, 32·1. Calc.: Mo, 17·2; Cl, 31·8%. For Rb_3MoCl_6, found: Mo, 16·9; Cl, 37·4. Calc.: Mo, 17·0; Cl, 37·7%. For Cs_3MoCl_6, found: Mo, 13·5; Cl, 29·9. Calc.: Mo, 13·6; Cl, 30·1%).

General Properties of the Complex Salts.—The salts of potassium and ammonium are extremely soluble even in cold water and give intensely red solutions. The salts of cæsium are quite insoluble and those of rubidium nearly so. In alcohol and ether all are practically insoluble. The aqueous solutions have an acid reaction, due to hydrolysis, which is accelerated by warming and results ultimately in the precipitation of the hydroxide of molybdenum. All the salts have pronounced reducing properties.

Physico-chemical Measurements.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water. If $K_3[MoCl_6]$ represents the correct formulation for tripotassium molybdenum hexachloride, four ions should be present in solution, and the apparent molecular weight, when ionisation is complete, should be 106·6; whilst diammonium molybdenum pentachloride, represented by $(NH_4)_2[MoCl_5,H_2O]$, should yield three ions and give an apparent molecular weight of 109·2.

TABLE I.

G. of substance per 100 g. water.	Conc. in mols. per 1000 g. water.	Osmotic factor.	Apparent mol. wt.
	Tripotassium molybdenum hexachloride.		
0·498	0·01170	3·86	110·3
0·829	0·01947	3·68	116·0
1·470	0·03453	3·54	120·5
3·045	0·07153	2·55	167·0
	Diammonium molybdenum pentachloride.		
0·863	0·02635	3·10	105·6
1·484	0·04532	2·92	112·2
2·115	0·06460	2·81	116·8
5·391	0·1646	2·31	141·7

The results (Table I) furnish strong evidence in favour of the suggested formulations, although it was found that the substances underwent continuous hydrolysis in solution, as illustrated by the data (Table II) for a solution of tripotassium molybdenum hexachloride at a concentration of 0·07153 mol. per 1000 g. of water.

TABLE II.

Time after dissolving (mins.)	—	10	30	37	45	53	73	155
Apparent mol. wt. ...	167·0	158·2	146·8	146·0	142·7	139·8	135·5	117·3
Osmotic factor	2·55	2·70	2·91	2·92	2·99	3·05	3·18	3·64

After a considerable time, the hydroxide of molybdenum separated.

Molecular-conductivity Determinations.—Further evidence for the existence of these complex ions was obtained by determinations of the molecular conductivity. Whilst salts of the type R_3MoCl_6 gave results—immediately after dissolving—similar to those for a quaternary electrolyte, complexes of the type R_2MoCl_5,H_2O were analogous to typical ternary electrolytes. Table III gives the values of μ for various dilutions at 1° when $t = 0$ min., and for comparison the values of the molecular conductivities at 1° of typical salts are given in Table IV.

TABLE III.

	K_3MoCl_6.					$(NH_4)_3MoCl_6,H_2O$.		
Dilution (litres per mol.)	15·67	58·97	95·84	153·3	222·0	48·11	66·44	157·9
μ	155	195	220	230	245	208	210	225
	$(NH_4)_2MoCl_5,H_2O$.					K_2MoCl_5,H_2O.		
Dilution (litres per mol.)	16·37	33·76	54·96	101·4	251·3	21·19	58·31	94·08
μ	107	110	132	140	175	113	140	142

TABLE IV.

Dilution (litres per mol.).	16.	32.	64.	128.	256.
KCl.	75·2	77·3	79·2	80·6	81·8
K_2SO_4.				164	172
$K_3Fe(CN)_6$.	204·3	219·6	232·2	247·2	259·2
$K_3W(CN)_8$.	201·9	216·0	229·2	243·6	255·6
$K_4Fe(CN)_6$.				292	316

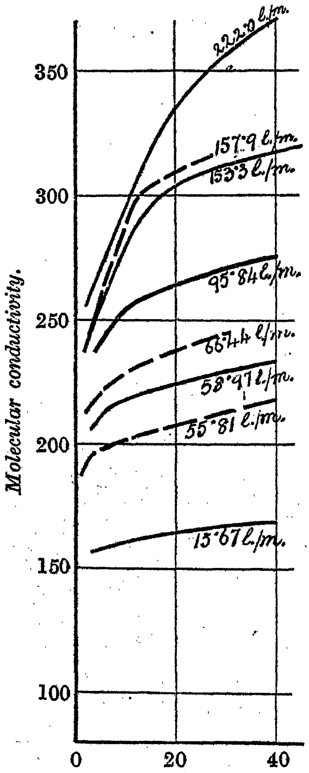
However, as was anticipated from the molecular-weight determinations, the conductivities increased with time, as is seen from Figs. 1 and 2, in which molecular conductivities are plotted against time for various dilutions (as litres per mol., indicated as l./m.) of the two types of salt.

Isolation of Double Salts of Molybdenyl Monochloride.

It was noticed, during the preparation of tripotassium molybdenum hexachloride and in attempts to prepare dipotassium molybdenum pentachloride, that solutions containing tervalent molybdenum of a low acid concentration, tended to give rise to molybdenyl monochloride, which had previously been isolated from solutions of high molybdenum content, by precipitation in acetone (J., 1924, **125**, 2372).

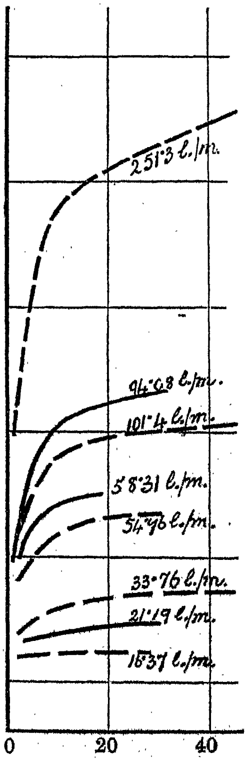
Preparation of Potassium Molybdenyl Dichloride.—350 C.c. of the green solution containing tervalent molybdenum (35 g. MoO_3) were concentrated to *ca.* 120 c.c. and re-electrolysed for an hour to ensure that all the molybdenum was tervalent. 250 C.c. of a 10% solution of potassium chloride were then added and the whole was concentrated nearly to dryness under reduced pressure at 70°. The red salt formed was then removed and the filtrate treated with alcohol, whereby a bright yellow substance was precipitated. This was filtered, washed with alcohol, and dried in a vacuum. It was slowly soluble in water to a reddish-brown solution and after a time the solid turned greenish-brown (Found: Mo, 36·0; Cl, 26·8; K, 14·3. $KMoOCl_2,2{\cdot}5H_2O$ requires Mo, 36·0; Cl, 26·6; K, 14·6%). The true hydrate is probably $KMoOCl_2,3H_2O$.

FIG. 1.



Conductivity of salts of type $R_3[MoCl_6]$.

FIG. 2.



Conductivity of salts of type $R_2[MoCl_5,H_2O]$

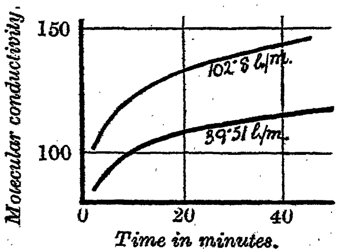
—— = K salts. — — = NH_4 salts.

Valency. This was determined by titration with standard permanganate in the presence of manganous phosphate. The valency of the molybdenum is given by $(6 - 3w_1/w_2)$, where w_1 is the percentage of molybdenum calculated from the titration, assuming that it is tervalent, and w_2 is the percentage of molybdenum found by gravimetric means. Here $w_1 = 35{\cdot}56$ and $w_2 = 36{\cdot}0$; hence the valency is 3.

Conductivity at 1°. The increase of molecular conductivity with time is illustrated in Fig. 3, with the same conventions as for Figs. 1 and 2. These results indicate, by analogy with potassium chloride (Table IV) that two ions are present in solution and that rapid hydrolysis occurs. Thus the new compound is shown to be $K[MoOCl_2,3H_2O]$.

By similar treatment of the green solution with ammonium chloride, a slightly impure substance was obtained, which was probably $(NH_4)[Mo(OH)Cl_3,2H_2O]$, and was shown to contain tervalent molybdenum.

FIG. 3.



Conductivity of $K[MoOCl_2,3H_2O]$.

The Replacement of the Halogen Units in the Complex Salts.

Chilesotti (*Gazzetta*, 1905, **34**, ii, 493), by double decomposition of the tripotassium molybdenum hexachloride and potassium thiocyanate, has prepared the complex salt $K_3Mo(CNS)_6$, whilst, by the action of hydrofluoric acid on the complex chlorides (Rosenheim and Li, *loc. cit.*), complex fluorides have been prepared. In view of the possibility of replacing the six chlorine atoms by three chelate groups such as the oxalato-, salicylato-, or phthalato-group the reactions between the complex chlorides and the alkali salts of oxalic, salicylic, and phthalic acids were investigated. In no case, however, was a complex salt obtained. Instead, the reactions yielded the co-ordination compounds $[Mo(OH)(OH{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2,H_2O]$ and $[Mo(OH)(O{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}O),3H_2O]$ and an impure oxalate of the latter type.

Reaction with Sodium Salicylate.—A concentrated aqueous solution containing 2 g. (1 mol.) of diammonium molybdenum pentachloride and 1 g. (2 mols.) of sodium salicylate, was warmed to 70° in an atmosphere of nitrogen. The solution gradually darkened and finally became greenish-brown, a brown precipitate being formed. This was washed several times with air-free water in a nitrogen atmosphere and dried in a vacuum. The substance was dark-brown, insoluble in water, but soluble in alcohol giving a brown solution, and in alkaline hydroxides to a yellow solution.

The molybdenum was estimated by precipitation (as above) and also by direct ignition to the trioxide. The carbon and hydrogen were estimated by combustion in oxygen [Found: Mo, 23·5; C, 41·5; H, 3·3. $Mo(OH)(OH{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2,H_2O$ requires Mo, 23·7; C, 41·5; H, 3·2%].

The same compound results from the reaction between sodium salicylate and the other complex chlorides.

The solubility of this substance in alkaline hydroxides indicates a probable acidic structure, which can be represented by the co-ordination formula $[MoO,(O{\cdot}OC{\cdot}C_6H_4{\cdot}OH)_2,H_2O]H$, in which the molybdenum has a co-ordination number of six.

Reaction with Disodium Phthalate.—By warming equimolecular proportions of the complex salt and disodium phthalate in concentrated solution, a brown phthalate was prepared of which the analysis indicates the constitution $Mo(OH)[C_6H_4(CO{\cdot}O)_2],3H_2O$ (Found: Mo, 29·2; C, 29·1; H, 3·4. Calc.: Mo, 29·0; C, 29·0; H, 3·35%).

Like the salicylate, the new substance is insoluble in water and soluble in alkaline hydroxides, and probably has an acidic structure in accordance with the formulation $[MoO{\cdot}(C_6H_4(CO{\cdot}O)_2),3H_2O]H$.

Reaction with Ammonium Oxalate.—On warming a concentrated solution containing the complex salt and ammonium oxalate, the liquid turned brown and finally greenish-brown, but no insoluble compound was formed. The addition of the solution to alcohol resulted in the precipitation of a brown substance which, after freeing from ammonium chloride by washing with aqueous alcohol, gave analyses which showed that, although ammonium oxalate was still present as impurity, the substance was probably

$$Mo(OH)(C_2O_4),3H_2O,$$

identical with the oxyoxalate previously isolated (J., 1925, **127**, 1311).

Reaction of the Complex Salts with Liquid Ammonia.

Attempts to replace the chlorine in the red salts by the NH_3 group proved unsuccessful, but it was shown that diammonium molybdenum pentachloride takes up ammonia to give an unstable monoammine, which may be written as $(NH_4)_2[MoCl_5,NH_3]H_2O$.

About 15 c.c. of liquid ammonia were added to 2—3 g. of the above complex chloride contained in a dry tube surrounded by ether and solid carbon dioxide. The reaction mixture was well stirred and the supernatant liquid then decanted off. The remaining solid was treated similarly with a further quantity of liquid ammonia to extract any ammonium chloride formed. After repeated washing with dry acetone to remove excess of ammonia, the solid mass was dried in an evacuated desiccator containing calcium chloride, and immediately analysed [Found: Mo, 26·7; Cl, 49·6; NH_4, 15·1; Mo : NH_4 : Cl = 1 : 3·01 : 5·03. $(NH_4)_2MoCl_5,NH_3,H_2O$ requires

Mo, 27·9; Cl, 51·5; NH_4, 15·7. $(NH_4)_2MoCl_5,NH_3,2H_2O$ requires Mo, 26·5; Cl, 49·0; NH_4, 14·9%]. The true hydrate when freshly prepared is probably $(NH_4)_2[MoCl_5,NH_3]H_2O$.

This mauve-coloured ammine is extremely hygroscopic and undergoes rapid hydrolysis, ammonium chloride being liberated whilst the substance itself turns brown. It is readily soluble in water, producing a reddish-brown solution from which the hydroxide separates after a few minutes. It was therefore impossible to determine its molecular conductivity.

On treatment with concentrated hydrochloric acid, the ammine dissolved, producing a brilliant blue coloration. On dilution the solution turned green and finally pink, owing, in all probability, to the re-formation of the original red complex chloride, with liberation of ammonium chloride.

An attempt was made to isolate the blue substance by passing hydrogen chloride into the acid solution of the ammine, maintained at the low temperature of the mixture of solid carbon dioxide and ether. A greenish-blue substance was precipitated, which, after washing with alcohol to remove hydrochloric acid, turned greenish-grey. In water, it gave a greenish-blue solution, which rapidly turned pink. The analytical figures were not in agreement with any definite formula.

Liquid ammonia does not appear to react with the tripotassium molybdenum hexachloride, thus supporting the view that the ammonia replaces the molecule of water in diammonium molybdenum pentachloride.

Discussion.

The results of the physico-chemical measurements, together with the isolation of co-ordination compounds of the formulæ

$$K[MoOCl_2,3H_2O],\quad [MoO,C_6H_4(CO\cdot O)_2,3H_2O]H$$

and $[MoO,(OH\cdot C_6H_4\cdot CO\cdot O)_2,H_2O]H$, can be explained on the assumption that the complex salts undergo ionisation and hydrolysis in accordance with the following scheme:

$$\begin{aligned} R_3[MoCl_6] + H_2O &\rightleftharpoons R_2[MoCl_5,H_2O] + RCl. \\ R_2[MoCl_5,H_2O] + H_2O &\rightleftharpoons R[MoCl_4,2H_2O] + RCl. \\ R[MoCl_4,2H_2O] + H_2O &\rightleftharpoons MoCl_3,3H_2O + RCl. \\ MoCl_3,xH_2O &\rightleftharpoons MoCl_2(OH) + HCl + (x-1)H_2O. \\ MoCl_2(OH) &\rightleftharpoons MoOCl + HCl. \end{aligned}$$

The existence of the double salts R_3MoCl_6 and R_2MoCl_5,H_2O is evidence of the presence of $MoCl_3$; the salicylato- and phthalato-compounds are derived from the intermediate $MoCl_2(OH)$; whilst MoOCl and its complex salts have been isolated.

It is of interest to note, in the case of the complex chlorides R_3MoCl_6,R_2MoCl_5,H_2O, and $KMoOCl_2$,$3H_2O$, and also of the insoluble molybdenyl salicylate and phthalate, that the molybdenum atom is associated with 51 electrons, 3 less than the number required for an inert-gas structure. In this respect, molybdenum shows a close analogy to chromium in its complex salts.

Here is an excellent illustration of the fact that co-ordination compounds may be stable in cases where the central atom has not an inert-gas structure, provided that the associating units are regularly distributed. Nevertheless, the complex compounds of tervalent molybdenum do not exhibit the stability of the complex cyanides of quadrivalent molybdenum, $R_4[Mo(CN)_8]$, in which the central atom has an inert-gas structure.

The authors wish to express their thanks for the award of a Priestley Scholarship to one of them (W. R. B.) and to the Chemical Society and Messrs. Brunner Mond and Co., Ltd., for grants in aid of this investigation.

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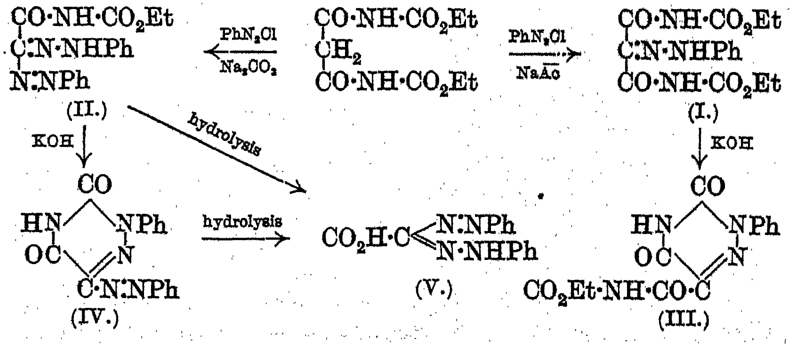
[*Received, December 23rd*, 1926.]

LXXVII.—*The Reaction between Diazonium Salts and Malonyldiurethane.*

By MARTHA ANNIE WHITELEY and DOROTHY YAPP.

MALONYLDIURETHANE condenses with benzenediazonium salts, yielding the *hydrazone* (I) or the *formazyl* derivative (II) according to whether the reaction is carried out in the presence of acetic acid or sodium carbonate, respectively. Each of these compounds



undergoes internal condensation by the action of potassium hydroxide whereby alcohol is eliminated between the ethoxyl group of the urethano-radical and the imino-hydrogen of the hydrazone group, yielding respectively the *carbourethane* (III) and the *benzeneazo-derivative* (IV) of 3 : 5-*diketo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine*. On hydrolysis with hot potassium hydroxide solution, the formazyl compound (II) and the benzeneazotriazine (IV) each yield formazylcarboxylic acid (V).

When the benzenediazonium salt in the above reactions is replaced by certain substituted derivatives, it is found that the nature of the substituent radical and its position in the benzene ring affect the course of the reaction: the *p*-toluene- and the *o*-nitrobenzene-diazonium salt each yield both the hydrazone and the formazyl compound, from which the triazine compounds can be obtained; whereas the *p*-nitrobenzenediazonium salt yields the hydrazone in two isomeric forms, but no formazyl compound, and each of the isomeric hydrazones yields the same triazine compound; *m*-nitrobenzenediazonium salt yields the hydrazone only, from which at present no triazine compound has been obtained.

In respect of forming a hydrazone and not an azo-compound by the action of benzenediazonium acetate, malonyldiurethane resembles malonic acid, barbituric acid and other compounds containing the keto-methylene group (compare Meyer, *Ber.*, 1888, **21**, 118; 1891, **24**, 1241; v. Pechmann, *Ber.*, 1892, **25**, 3175; Kuhling, *Ber.*, 1891, **24**, 4140; 1898, **31**, 1972; Bamberger and Wheelwright, *Ber.*, 1892, **25**, 3201), and this constitution of the compound was confirmed by its preparation from monobromomalonyldiurethane and phenylhydrazine, when simultaneous condensation and oxidation occurred (compare v. Pechmann, *loc. cit.*). That

$$\begin{array}{ccr} (\mathrm{CO_2Et\cdot NH\cdot CO})_2\mathrm{CHBr} & \xrightarrow{\mathrm{PhNH\cdot NH_2}} & [(\mathrm{CO_2Et\cdot NH\cdot CO})_2\mathrm{CH\cdot NH\cdot NHPh}] \\ & & \downarrow \\ & & (\mathrm{CO_2Et\cdot NH\cdot CO})_2\mathrm{C{:}N\cdot NHPh} \end{array}$$

this reaction is a general one was shown by the preparation of mesoxamide phenylhydrazone by condensation of (i) dibromomalonamide with phenylhydrazine as described by Ruhemann and Orton (J., 1895, **67**, 1003); (ii) monobromomalonamide with phenylhydrazine; and (iii) benzenediazonium acetate with malonamide:

$$\begin{array}{ll} \left.\begin{array}{l} (\mathrm{CO\cdot NH_2})_2\mathrm{CBr_2} \\ (\mathrm{CO\cdot NH_2})_2\mathrm{CHBr} \end{array}\right\} & \xrightarrow{\mathrm{PhNH\cdot NH_2}} \\ (\mathrm{CO\cdot NH_2})_2\mathrm{CH_2} & \xrightarrow[\mathrm{PhN_2Cl,Na\overline{Ac}}]{} \end{array} (\mathrm{CO\cdot NH_2})_2\mathrm{C{:}N\cdot NHPh}.$$

The formation of the formazyl compound when benzenediazonium chloride is added to a solution of malonyldiurethane in sodium carbonate solution is probably due to the further action of the diazonium compound on the phenylhydrazone of glyoxalylurethane produced by the hydrolysis of one of the carbourethano-groups and loss of carbon dioxide from the resulting acid:

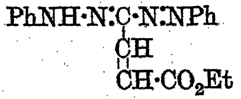
$$\begin{tikzcd}(CO\cdot NH\cdot CO_2Et)_2C{:}N\cdot NHPh \arrow[r, "\text{hydrolysis}"] & (CO\cdot NH\cdot CO_2Et)C(CO_2H){:}N\cdot NHPh \arrow[d, "-CO_2"] \\ (CO\cdot NH\cdot CO_2Et)C(N{:}NPh){:}N\cdot NHPh & (CO\cdot NH\cdot CO_2Et)CH{:}N\cdot NHPh \arrow[l, "PhN_2\cdot OH"']\end{tikzcd}$$

In respect of the above reactions, malonyldiurethane closely resembles malonic acid (v. Pechmann, *loc. cit.*; Busch and Wolbring, *J. pr. Chem.*, 1905, **72**, 366), but whereas the final product of the action of diazonium salts on malonic acid is formazylazobenzene, owing to the readiness with which formazylcarboxylic acid loses carbon dioxide, its urethane derivative resists hydrolysis and forms a stable six-membered ring by loss of alcohol.

There are numerous cases recorded in the literature of internal ring formation in hydrazones and formazyl compounds (see Bamberger and Lorenzen, *Ber.*, 1892, **25**, 3539; Bamberger and de Gruyter, *Ber.*, 1893, **26**, 2385, 2783; Bamberger and Witten, *Ber.*, 1894, **27**, 2786; v. Pechmann, *ibid.*, p. 1679; v. Pechmann and Runge, *ibid.*, p. 2920; Fichter and Schiess, *Ber.*, 1900, **33**, 747), but the researches of Henrich and his collaborators on the formazyl and arylazohydrazone derivatives yielded by glutaconic acid and its esters appear to have a direct bearing on the work described in this paper. These authors found that glutaconic acid reacts with benzenediazonium chloride (2 mols.) in the presence of sodium acetate to form formazylacrylic acid, $CO_2H\cdot CH{:}CH\cdot C(N{:}NPh){:}N\cdot NHPh$ (Henrich and Thomas, *Ber.*, 1907, **40**, 4924); whilst ethyl glutaconate under similar conditions reacts with the diazonium salt (1 mol.) to form a compound which has the constitution of the azo-compound, $CO_2Et\cdot CH{:}CH\cdot CH(CO_2Et)\cdot N{:}NPh$, or that of the tautomeric hydrazone, $CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NHPh$; and when an excess of the diazonium salt is used the arylazohydrazone, ethyl α-keto-γ-benzeneazoglutaconate phenylhydrazone,

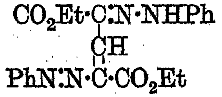
$$CO_2Et\cdot C(N{:}NPh){:}CH\cdot C(CO_2Et){:}N\cdot NHPh,$$

is formed, and this compound differs from the others in that it very readily loses a molecule of alcohol, even on boiling with alcohol, to form the ring compound, ethyl 1-phenyl-5-benzeneazopyridazin-6-one-3-carboxylate, $CH{<}\begin{matrix}C(CO_2Et)=N\\C(N{:}NPh)\cdot CO\end{matrix}{>}NPh$ (Henrich, Reichenburg, Nachtigall, Thomas, and Baum, *Annalen*, 1910, **376**, 125). In view of the readiness with which the phenylhydrazone of mesoxalyldiurethane and the urethane derivative of formazylglyoxylic acid form rings by the loss of alcohol, and in this respect resemble the arylazohydrazone derivative of ethyl glutaconate, it is the more remarkable that formazylacrylic acid and its ethyl ester are such stable substances and show no tendency to form rings. A simple explanation of this anomalous behaviour would be afforded if it were assumed that the stable forms of these compounds have the *trans*-configuration in respect of the carbethoxy- and hydrazone-groups, whilst that of the arylazohydrazone is *cis*:



$$\begin{array}{l} \mathrm{PhNH{\cdot}N{:}C{\cdot}N{:}NPh} \\ \qquad\qquad \mathrm{CH} \\ \qquad\qquad \mathrm{CH{\cdot}CO_2Et} \end{array}$$

Ethyl *trans*-formazylacrylate.



$$\begin{array}{l} \mathrm{CO_2Et{\cdot}C{:}N{\cdot}NHPh} \\ \qquad\qquad \mathrm{CH} \\ \mathrm{PhN{:}N{\cdot}C{\cdot}CO_2Et} \end{array}$$

Ethyl *cis*-α-keto-γ-benzeneazoglutaconate phenylhydrazone.

The stability of the first product of the action of diazonium acetate on ethyl glutaconate, a compound which can even be distilled without decomposition, may be regarded as evidence of its having the azo-structure, but if it is a hydrazone it probably has the *trans*-configuration.

With reference to the part played by the nature and position of the radical in substituted benzenediazonium derivatives in inhibiting the formation of formazyl derivatives from hydrazones, or of ring compounds from hydrazones or formazyl compounds, the evidence at present available is scanty and of a conflicting nature. The results obtained with malonyldiurethane indicate that a positive substituent in the ortho- or a negative substituent in the para-position offers no hindrance to the formation of the formazyl compound (II) or of the ring compound (III), but that a positive substituent in the para-position prevents the formation of the formazyl, but not of the ring compound, whilst a positive substituent in the meta-position inhibits both formazyl and ring formation. Busch and Wolbring (*loc. cit.*) found that malonic acid gives chiefly the substituted hydrazone of glyoxylic acid and very little of the formazyl hydride when it condenses with certain ortho-substituted derivatives of benzenediazonium salts, such as *o*-nitro-, *o*-chloro-, *o*-bromo-, or *o*-iodo-derivatives, whilst the formazyl compound is the only product when malonic acid condenses with *p*-bromo- or *m*-nitro-benzenediazonium salts, and the chief product when it condenses with *p*-nitroaniline. Henrich and his collaborators (*loc. cit.*), who studied the relative ease of ring formation in the substituted arylazohydrazones of ethyl glutaconate, found that it depended both on the nature and on the position of the substituent in the benzene ring. The more negative the substituent the more readily did ring formation occur, provided that the substituent was not in the ortho-position, as ortho-substitution presented a steric hindrance to the elimination of alcohol.

EXPERIMENTAL.

I. *Phenylhydrazone of Mesoxalyldiurethane* (I).—(i) Into a solution of 5 g. (1 mol.) of malonyldiurethane in 200 c.c. of dilute aqueous sodium acetate cooled in ice, was slowly stirred a cold solution of benzenediazonium acetate prepared by diazotising 1·8 g. (1 mol.) of aniline dissolved in 10 c.c. of dilute hydrochloric acid (1 : 1) and adding excess of sodium acetate. The mixture was kept for 2 hours at 0—5° and the *hydrazone* separated in a crystalline form (yield, 4·8 g.). It is soluble in acetic acid, formic acid, or chloroform, but insoluble, or nearly so, in all the other ordinary organic solvents, and crystallises from acetic acid in pale yellow needles, m. p. 203° (decomp.) (Found: C, 51·3; H, 5·15; N, 16·1. $C_{15}H_{18}O_6N_4$ requires C, 51·4; H, 5·1; N, 16·0%).

(ii) The same compound was also prepared by heating at 100° an alcoholic solution of monobromomalonyldiurethane (1 mol.) and phenylhydrazine (1 mol.).

By replacing the aniline in preparation (i) above by its equivalent of the corresponding base, the following substituted phenylhydrazones of mesoxalyldiurethane were prepared:

(1) The o-*nitrophenylhydrazone*,

$$(CO\cdot NH\cdot CO_2Et)_2C\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

is soluble in acetic acid, acetone, or chloroform, sparingly soluble in ethyl or methyl alcohol or benzene, and insoluble in petroleum; it crystallises from acetic acid in thin, yellow needles, m. p. 208° (decomp.) (Found: N, 17·9. $C_{15}H_{17}O_8N_5$ requires N, 17·7%).

(2) The m-*nitrophenylhydrazone* is very readily soluble in acetic acid, but otherwise resembles the ortho-compound in its solubility. It crystallises from formic acid in very pale yellow needles, m. p. 215° (Found: N, 17·6%).

(3) The p-*nitrophenylhydrazone* crystallises from acetic acid in pale yellow needles, m. p. 218° (decomp.) (Found: N, 17·5%). An isomeric form of this hydrazone is obtained when the condensation of malonyldiurethane with *p*-nitrobenzenediazonium salt is effected in the presence of sufficient sodium carbonate to produce a neutral or slightly alkaline reaction. The *isomeride* crystallises in orange-coloured needles, m. p. 208° (decomp.) (Found: C, 45·4; H, 4·5; N, 17·8. $C_{15}H_{17}O_8N_5$ requires C, 45·5; H, 4·3; N, 17·7%).

(4) The p-*tolylhydrazone*, $(CO\cdot NH\cdot CO_2Et)_2C\colon N\cdot NH\cdot C_7H_7$, is readily soluble in all the usual organic solvents with the exception of petroleum; it crystallises from alcohol in pale yellow needles, m. p. 186° (Found: N, 15·5. $C_{16}H_{20}O_6N_4$ requires N, 15·4%).

II. *Urethane Derivative of Formazylcarboxylic Acid* (II).—Into a cold solution of 5 g. (1 mol.) of malonyldiurethane and 8·8 g. (2·5 mols.) of sodium carbonate in 200 c.c. of water was stirred one-half of a cold solution of benzenediazonium chloride, prepared by diazotising 3·6 g. (2 mols.) of aniline in 20 c.c. of dilute hydrochloric acid (1 : 1). The mixture was kept cold and after 2 hours the red precipitate (4·1 g.) was removed by filtration and the filtrate treated with the remainder of the diazonium solution; a further quantity (1 g.) of the product was then obtained. The product consisted of the *urethane* derivative of *formazylcarboxylic acid* (II) containing a small quantity of the triazine compound (III); separation was effected by boiling with water, in which the triazine compound is soluble. The urethane derivative of formazylcarboxylic acid is soluble in all the usual organic solvents except petroleum, it crystallises from alcohol in bright red plates, m. p. 159° (decomp.), and it gives a deep purple coloration when dissolved in concentrated sulphuric acid (Found : C, 60·1; H, 5·1; N, 20·9. $C_{17}H_{17}O_3N_5$ requires C, 60·2; H, 5·0; N, 20·6%). It undergoes hydrolysis when boiled with 10% potassium hydroxide solution, yielding formazylcarboxylic acid (V), m. p. 162° (v. Pechmann, *Ber.*, 1892, **25**, 3175, gives m. p. 162—163°) (Found : C, 63·2; H, 4·6; N, 20·7. Calc. : C, 62·7; H, 4·5; N, 20·9%).

The following substituted formazyl derivatives were similarly prepared :

(1) The *urethane* derivative of *di*-o-*nitroformazylcarboxylic acid*, $CO_2Et\cdot NH\cdot CO\cdot C(N{:}N\cdot C_6H_4\cdot NO_2){:}N\cdot NH\cdot C_6H_4\cdot NO_2$, is soluble in all the ordinary organic solvents with the exception of petroleum, and of formic acid, in which it decomposes; it crystallises from acetic acid in red plates with a green reflex, containing acetic acid of crystallisation and melting at 105°, and develops a deep blue coloration when dissolved in concentrated sulphuric acid (Found : C, 46·8; H, 3·9; N, 19·9. $C_{17}H_{15}O_7N_7,C_2H_4O_2$ requires C, 46·6; H, 3·9; N, 20·0%).

(2) The *urethane* derivative of *di*-p-*tolylformazylcarboxylic acid*, $CO_2Et\cdot NH\cdot CO\cdot C(N{:}N\cdot C_7H_7){:}N\cdot NH\cdot C_7H_7$, resembles the *o*-nitro-derivative in its solubility, and crystallises from alcohol in bright red needles that melt at 153°, and give a deep blue coloration with concentrated sulphuric acid (Found : C, 62·3; H, 5·9; N, 19·1. $C_{19}H_{21}O_3N_5$ requires C, 62·15; H, 5·7; N, 19·1%). This compound is hydrolysed by boiling with 10% potassium hydroxide solution, yielding *di*-p-*tolylformazylcarboxylic acid*,

$$HO_2C\cdot C(N{:}N\cdot C_7H_7){:}N\cdot NH\cdot C_7H_7,$$

which crystallises from acetic acid in red, rhomboidal crystals, m. p. 182° (Found : N, 19·1. $C_{16}H_{16}O_2N_4$ requires N, 18·9%).

III. The *urethane* derivative of 3 : 5-*diketo-2-phenyltetrahydro-1 : 2 : 4-triazine-6-carboxylic acid* (III) was prepared by dissolving the phenylhydrazone of mesoxalyldiurethane (I) in warm 10%

aqueous potassium hydroxide and subsequently acidifying the solution with a dilute mineral acid. It is soluble in hot water and crystallises from very dilute alcohol in pale buff-coloured, feathery crystals, m. p. 203° (decomp.) (Found: C, 51·7 *; H, 4·05; N, 18·5. $C_{13}H_{12}O_5N_4$ requires C, 51·3; H, 3·9; N, 18·4%).

The following substituted triazine derivatives were similarly prepared:

(1) The *urethane* derivative of 3 : 5-*diketo*-2-p-*nitrophenyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* is obtained from each of the two isomeric forms of the *p*-nitrophenylhydrazone of mesoxalyldiurethane; it crystallises in garnet-red prisms, m. p. 205° (Found: N, 19·9. $C_{13}H_{11}O_7N_5$ requires N, 20·05%).

(2) The *urethane* derivative of 3 : 5-*diketo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* crystallises from dilute alcohol in pale buff, silky needles, m. p. 218° (decomp.) (Found: C, 53·0 *; H, 4·5; N, 17·6. $C_{14}H_{14}O_5N_4$ requires C, 52·9; H, 4·4; N, 17·6%).

IV. 3 : 5-*Diketo*-6-*benzeneazo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine* (IV) was prepared by two methods: (i) by dissolving the urethane derivative of formazylcarboxylic acid (II) in warm alcoholic potassium hydroxide, diluting the solution with water, and acidifying the mixture with dilute hydrochloric acid; (ii) by the prolonged boiling of the same formazyl compound in xylene solution. The *triazine* crystallises from alcohol in orange needles, m. p. 256° (decomp.), that develop a deep red colour when dissolved in concentrated sulphuric acid (Found: C, 61·9 *; H, 3·8; N, 24·0. $C_{15}H_{11}O_2N_5$ requires C, 61·4; H, 3·75; N, 23·9%). This compound is hydrolysed by boiling with 10% potassium hydroxide solution, yielding formazylcarboxylic acid, m. p. 162°.

The following substituted triazine derivatives were similarly prepared:

(1) 3 : 5-*Diketo*-2-o-*nitrophenyl*-6-o-*nitrobenzeneazotetrahydro*-1:2:4-*triazine* crystallises from acetic acid in red, rhomboidal crystals, m. p. 224° (decomp.) (Found: N, 25·4. $C_{15}H_9O_6N_7$ requires N, 25·6%).

(2) 3 : 5-*Diketo*-6-p-*tolueneazo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine* crystallises from alcohol in orange-red needles, m. p. 246° (Found: C, 64·3 *; H, 4·8; N, 21·75. $C_{17}H_{15}O_2N_5$ requires C, 63·55; H, 4·7; N, 21·8%). When this compound is hydrolysed by hot potassium hydroxide solution the ring is ruptured in two places and di-*p*-tolylformazylcarboxylic acid, m. p. 182°, is formed.

The phenylhydrazone of mesoxamide, $(CO{\cdot}NH_2)_2C{:}N{\cdot}NHPh$, was prepared by Ruhemann and Orton (J., 1895, **67**, 1005) by heating an alcoholic solution of dibromomalonamide with the required quantity of phenylhydrazine; it crystallises in long, yellow needles, m. p. 232—233°. The same compound was obtained (i) by heating an alcoholic solution of monobromomalonamide (Backes, West, and Whiteley, J., 1921, **119**, 364) with one equivalent of phenylhydrazine (Found: C, 51·9; H, 4·95; N, 27·2. Calc.: C, 52·4; H, 4·85; N, 27·2%); and (ii) by the action of benzenediazonium chloride on an aqueous solution of malonamide containing excess of sodium acetate; the product crystallised from alcohol in long, yellow needles that melted at 232° and did not depress the melting point of the compound prepared by Ruhemann and Orton's method.

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* The high values obtained for carbon in the analysis of triazine compounds have been observed by Widman (*Ber.*, 1893, **26**, 2612).

One of us (M. A. W.) desires to thank the Council of the Royal Society for a grant which has covered much of the cost of the materials required for this investigation.

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[*Received, January 5th,* 1927.]

NOTES.

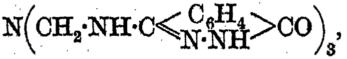
A Derivative of $\alpha\alpha'\alpha''$*-Triaminotrimethylamine.*

By FREDERIC BARRY KIPPING and FREDERICK GEORGE MANN.

IT has been shown by Ristenpart (*Ber.*, 1896, **29**, 2530) that molten phthal-β-bromoethylimide when treated with gaseous ammonia gives triphthalimidotriethylamine, $(C_6H_4{:}C_2O_2{:}N\cdot C_2H_4)_3N$, which on hydrolysis with hydrochloric acid furnishes ββ′β″-triaminotriethylamine trihydrochloride, $N(C_2H_4\cdot NH_2,HCl)_3$. This preparation has been improved by Mann and Pope (*Proc. Roy. Soc.*, 1925, [*A*], **109**, 444), who have also prepared γγ′γ″-triaminotripropylamine tetrahydrochloride similarly from phthal-γ-bromopropylimide (J., 1926, 489).

We have now investigated the stability of αα′α″-triaminotrimethylamine, $N(CH_2\cdot NH_2)_3$, by a similar series of reactions. Phthalbromomethylimide was prepared from phthalhydroxymethylimide by the method of Pucher and Johnson (*J. Amer. Chem. Soc.*, 1922, **44**, 817), this being a great improvement on the older method of Sachs (*Ber.*, 1898, **31**, 1225). A solution of phthalbromomethylimide (100 g.) in dry xylene (500 c.c.) was boiled under reflux for 8 hours while a stream of dry ammonia gas was passed through it. The solid product which had separated was then filtered, crushed, and extracted with water and alcohol, and the insoluble residue was recrystallised from glacial acetic acid. *Triphthalimidotrimethyl-*

amine, $(C_6H_4{:}C_2O_2{:}N{\cdot}CH_2)_3N,CH_3{\cdot}CO_2H$, separated with a molecule of acetic acid in colourless prisms, m. p. 222—223° (22 g.) (Found: C, 62·8; H, 3·8. $C_{29}H_{22}O_8N_4$ requires C, 62·8; H, 4·0%). Recrystallisation from pyridine gave the free *triphthalimidotrimethylamine* in colourless prisms, m. p. 235° (Found: C, 65·8; H, 3·5; N, 11·2. $C_{27}H_{18}O_6N_4$ requires C, 65·6; H, 3·6; N, 11·3%). The molecule of acetic acid, which is slowly lost when the compound is heated in a vacuum at 100°, may be present as acetic acid of crystallisation, or may be united to the tertiary amine group to form an unstable acetate. The formation of an acetate is most improbable, however, in view of the very feebly basic properties of the tertiary amine group in triaminotriethylamine (Mann and Pope, *loc. cit.*).

When triphthalimidotrimethylamine (10 g.) was heated gently under reflux with hydrochloric acid (1 : 1 by vol.; 300 c.c.), a complete solution was obtained after about 8 hours. This solution contained, however, only phthalic acid, formaldehyde, and ammonium chloride. Ing and Manske (J., 1926, 2348) have recently described a far less drastic method of hydrolysing phthalimido-compounds by treating them in alcoholic suspension with hydrazine hydrate. A suspension of triphthalimidotrimethylamine (3 g.) in alcohol (100 c.c.) was therefore heated on the water-bath with hydrazine hydrate (5 c.c. of 50% aqueous solution). The clear solution, which was rapidly obtained, soon deposited a white, gelatinous precipitate, which, after heating for 2 hours, was filtered off, washed, and recrystallised from alcohol. This compound, which did not melt below 330°, was probably *triphthalylhydrazidotriaminotrimethylamine*,  $N\left(CH_2{\cdot}NH{\cdot}C{<}^{C_6H_4}_{N\cdot NH}{>}CO\right)_3$, but was too unstable to be obtained pure (Found, after consecutive alcoholic recrystallisations: N, 25·5, 26·7. $C_{27}H_{24}O_3N_{10}$ requires N, 26·2%). When this product was treated with cold dilute hydrochloric acid, a thick suspension of phthalylhydrazide, $C_6H_4{:}C_2O_2{:}(NH)_2$ (Found: N, 17·4. Calc. for $C_8H_6O_2N_2$: 17·3%), separated with evolution of heat, whilst the solution contained formaldehyde and ammonium chloride.

It is clear from these results that $\alpha\alpha'\alpha''$-triaminotrimethylamine cannot be isolated owing to its ready hydrolysis to formaldehyde and ammonia, but is stable in the form of its triacyl derivatives. Its behaviour is thus closely akin to that of the parent methylenediamine, $CH_2(NH_2)_2$, which also hydrolyses readily into formaldehyde and ammonia, but gives stable diacetyl and dibenzoyl derivatives (Pulvermacher, *Ber.*, 1892, **25**, 310; Einhorn and Mauermayer, *Annalen*, 1905, **343**, 307) and also a stable diurethane,

$$CH_2(NH{\cdot}CO_2Et)_2$$

(Curtis, *J. pr. Chem.*, 1895, **52**, 225; Conrad and Hock, *Ber.*, 1903, **36**, 2206).

Phthalbromomethylimide unites vigorously with pyridine to give *phthalimidomethylpyridinium bromide*, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2{\cdot}NC_5H_5Br$, which, after recrystallisation from alcohol, is obtained in large, colourless prisms, m. p. (on rapid heating) 244° (Found: Br, 25·2. $C_{14}H_{11}O_2N_2Br$ requires Br, 25·1%). This quaternary ammonium bromide, when boiled with dilute hydrochloric acid (1 : 1 by vol.), gave pyridine, ammonia, phthalic acid, and formaldehyde.

Phthalbromomethylimide reacts violently with anhydrous diethylamine, and, even when the reaction occurs in dilute xylene solution, phthalimide is the chief product. Pucher and Johnson (*loc. cit.*) have shown that phthalimide is also produced by the action of potassium cyanide, ethyl sodioacetoacetate, or ethyl sodio-γ-diethoxyacetoacetate on phthalbromomethylimide, and the latter, they suggest, often acts as if it were a methyleneammonium bromide of constitution $C_6H_4{:}C_2O_2{:}N(Br){:}CH_2$. Its reactions with ammonia and pyridine described above are, however, those of the true phthalbromomethylimide, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2Br$.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 25th,* 1926.]

The Action of Nitrous Acid on ar-*Tetrahydro-α-naphthol and on 5 : 8- and 5 : 6(or 7 : 8)-Dihydro-α-naphthols.* By FREDERICK MAURICE ROWE AND ESTHER LEVIN.

SCHROETER's statement (*Annalen*, 1922, **426**, 104, 152) that nitrous acid converts *ar*-tetrahydro-α-naphthol into 4-nitroso-*ar*-tetrahydro-α-naphthol, greenish-yellow needles, m. p. 161—163° (decomp.), led the authors to re-examine the product of this reaction, yellow needles, m. p. 163° (decomp.), obtained by Green and Rowe (J., 1918, **113**, 965) and described as 4-nitro-*ar*-tetrahydro-α-naphthol. That this product was really the 4-nitroso-compound has now been proved as follows: An aqueous suspension of *ar*-tetrahydro-α-naphthaquinone was mixed with an aqueous solution of hydroxylamine hydrochloride, the mixture was kept for 24 hours and then rendered alkaline and filtered, and the filtrate was acidified. The precipitated *ar*-tetrahydro-α-naphthaquinoneoxime (4-nitroso-*ar*-tetrahydro-α-naphthol) crystallised from dilute alcohol in yellow needles, m. p. 163° (decomp.) (Found:* C, 68·1; H, 6·3; N, 7·8. Calc.: C, 67·8; H, 6·2; N, 7·9%) and was identical in all respects with Green and Rowe's "4-nitro"-compound. Further, the finely powdered compound, prepared in either way, was oxidised to the corresponding nitro-derivative by adding 2 g. in small portions at a time to a mixture of 3 c.c. of nitric acid (*d* 1·4) and 9 c.c. of water at 40°. 4-*Nitro*-ar-*tetrahydro*-α-*naphthol* crystallises from toluene in faintly coloured needles, m. p. 123°; it is not volatile with steam and forms yellowish-brown salts (Found: C, 62·2; H, 5·9; N, 7·3. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·2%).

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* To obtain accurate results, it was essential to carry out the combustions extremely slowly.

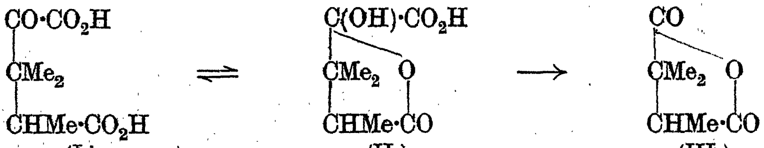
Finally, the products of the interaction of an aqueous solution of phenylhydrazine hydrochloride and a glacial acetic acid suspension of *ar*-tetrahydro-α-naphthaquinone, and of a mixture of 4-nitroso-*ar*-tetrahydro-α-naphthol and aniline acetate at the temperature of a boiling water-bath, were identical with benzeneazo-*ar*-tetrahydro-α-naphthol, prepared by coupling benzenediazonium chloride with *ar*-tetrahydro-α-naphthol (Jacobson and Turnbull, *Ber.*, 1898, **31**, 898).

Also the compounds described as 4-nitro-5 : 8-dihydro-α-naphthol and 4-nitro-5 : 6(or 7 : 8)-dihydro-α-naphthol (J., 1921, **119**, 2024) gave, on very slow combustion, results which show that they are really the 4-nitroso-compounds: 4-*Nitroso*-5 : 8-*dihydro*-α-*naphthol*, brownish-yellow needles, m. p. 161° (decomp.) (Found: C, 68·6; H, 5·2; N, 7·9. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1; N, 8·0%); 4-*nitroso*-5 : 6(or 7 : 8)-*dihydro*-α-*naphthol*, yellow needles, m. p. 162° (decomp.) (Found: C, 68·7; H, 5·3; N, 7·8. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1; N, 8·0%). These compounds are too sensitive to oxidation to permit their conversion into the corresponding nitro-derivatives with nitric acid; moreover, the dihydro-α-naphthylamines cannot be oxidised to dihydro-α-naphthaquinones (J., 1922, **121**, 1001).—THE UNIVERSITY, LEEDS. [*Received, December 8th, 1926.*]

LXXVIII.—*Ring-chain Tautomerism. Part XV. The Hydroxy-lactone Type.*

By EUGENE ROTHSTEIN and CHARLES WILLIAM SHOPPEE.

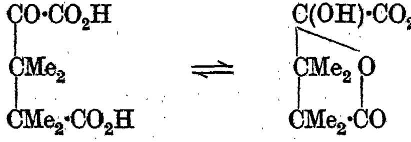
IN Part I of this series (Kon, Stevenson, and Thorpe, J., 1922, **121**, 654; see also Rothstein, Stevenson, and Thorpe, J., 1925, **127**, 1073), it was shown that the acid $C_8H_{12}O_5$ (Balbiano's acid) is a mixture of two tautomeric individuals (I and II). The evidence for the presence of the tautomeride (II) consisted in the fact that on treatment with *o*-phenylenediamine in acetic acid solution an acidic addition product, which was not a salt, was formed, and on heating this, or on boiling the two substances together, the usual quinoxaline derivative was formed. There was additional evidence for the existence of the hydroxy-lactone isomeride (II), inasmuch as the latter gave off carbon monoxide, with the formation of trimethylsuccinic anhydride (III), when heated above its melting point (*loc. cit.*).



(I.) (II.) (III.)

The authors have now investigated the methyl derivative (IV) of Balbiano's acid (Francis and Willsdon, J., 1913, **103**, 2238), because it seemed to them that the presence of the second *gem*-dimethyl group should stabilise the hydroxy-lactonic form (V) of the acid. This has been found to be the case.

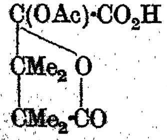
(IV.)



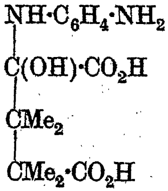
(V.)

When the acid (V) was titrated with baryta solution, it behaved as a monobasic acid. When it was boiled with *N*/100-baryta, the hydroxy-lactone ring underwent fission to the extent of about 40%. Similar treatment with *N*/10-baryta increased the fission to 95%, but complete fission could not be obtained. Balbiano's acid, under similar conditions, always yielded the normal barium salt (of the dibasic acid). The above figures were also obtained after the acid (V) had been esterified to the dimethyl ester and then regenerated by hydrolysis.

Another striking difference between the acid (V) and Balbiano's acid, indicating the difference in stability of the respective hydroxy-lactonic rings, is that the former yielded an *acetyl* derivative (VI) on treatment with acetic anhydride. This derivative decomposes sodium hydrogen carbonate and behaves as a monobasic acid on titration.

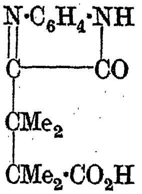


(VI.)



$$\begin{array}{l} \mathrm{NH{\cdot}C_6H_4{\cdot}NH_2} \\ \mid \\ \mathrm{C(OH){\cdot}CO_2H} \\ \mid \\ \mathrm{CMe_2} \\ \mid \\ \mathrm{CMe_2{\cdot}CO_2H} \end{array}$$

(VII.)



(VIII.)

Like Balbiano's acid, the compound (V) gives an *addition product* (VII) with *o*-phenylenediamine, and also the *condensation product*

(VIII). There is, however, an important distinction between the two compounds. Whereas the condensation product can be obtained from Balbiano's acid by boiling the acid itself with *o*-phenylenediamine, the only methods by which the corresponding derivative is formed from the tetramethyl acid are by heating the addition product, by fusing the acid and the phenylenediamine together, and by fusing the dimethyl ester with the same compound.

It is evident, therefore, that the hydroxy-lactone phase is the stable form of the tetramethyl compound, and, unlike Balbiano's acid, in solution this is not a tautomeric mixture of (IV) and (V). The presence of alkalis or acids, however, tends to shift the equilibrium in favour of the ketonic form.

It is therefore now possible to record the existence of three members of an homologous series, differing from one another in the possession of an additional methyl group, in which the influence of this group on the carbon tetrahedral angle is clearly demonstrated by the chemical and physical properties of the substances described. The ββ-dimethyl compound is static as a hydrated ketone, the ββγ-trimethyl acid (I and II) is a tautomeric mixture of the ketonic and the hydroxy-lactonic form, whilst, finally, the ββγγ-tetramethyl acid (V) is static as the hydroxy-lactone.

EXPERIMENTAL.

Hydroxy-lactone of α-Keto-ββγγ-tetramethylglutaric acid (V).—The acid was prepared from bromohydroxyphorone by the method of Francis and Willsdon (*loc. cit.*). After recrystallisation from toluene, or ethyl acetate and light petroleum, it melted at 140° (Found: C, 53·2; H, 6·9. Calc.: C, 53·4; H, 6·9%).

Titration with *N*/100-baryta solution gave *M*, 202, 204 [Calc.: *M* (monobasic), 202]. When the acid was boiled with *N*/100- and with *N*/10-baryta solution, and then titrated with *N*/20-hydrochloric acid, the values of *M* were 162 and 107, respectively. Balbiano's acid, both on direct and on back titration, gave the value *M*, 95 [Calc.: *M* (dibasic), 94].

When the acid was heated above its melting point, it yielded carbon monoxide (11·9 litres per g.-mol.), and tetramethylsuccinic anhydride was found in the residue.

The dimethyl ester, b. p. 170°/15 mm., was prepared by the action of methyl iodide on the disilver salt, or by Phelp and Tillotson's alcohol-vapour method. It crystallised from benzene, or from chloroform and ligroin, in plates, m. p. 103°. The ester could not be characterised by the formation of ketonic derivatives.

Acetyl Derivative of the Acid $C_9H_{14}O_5$ (VI).—The acid (V) was heated under reflux with acetic anhydride for one hour, and the excess of the latter was then removed in a vacuum desiccator containing potash. The product, twice crystallised from benzene and petroleum, formed stellate clusters of needles, m. p. 149° (Found : C, 54·0; H, 6·5; *M*, 241. $C_{11}H_{16}O_6$ requires C, 54·1; H, 6·6%; *M*, monobasic, 244).

Addition Product with o-*Phenylenediamine* (VII).—The acid (V) (0·5 g.), dissolved in the minimum of water, was treated with 10% excess of *o*-phenylenediamine, dissolved in glacial acetic acid. On warming and rubbing, a pale buff precipitate appeared, which separated from alcohol in plates, m. p. 160° (Found : C, 58·7; H, 7·1; N, 8·8. $C_{15}H_{22}O_5N_2$ requires C, 58·4; H, 7·1; N, 9·0%).

The substance decomposes sodium hydrogen carbonate, but not sodium hydroxide solution. When heated above its melting point, it loses water and yields the condensation product (VIII).

Condensation Product with o-*Phenylenediamine* (VIII).—(*a*) The acid (V) (0·5 g.) and *o*-phenylenediamine (0·3 g.) were fused together at 165° for ½ hour. After cooling, the product was treated with a small quantity of boiling alcohol; the almost colourless residue crystallised from acetic acid in tiny cubes, m. p. 238—239°. The alcoholic filtrate slowly deposited the addition compound as a buff precipitate.

(*b*) The dimethyl ester (0·4 g.) and *o*-phenylenediamine, similarly heated together, gave the same product.

The substance, after being crystallised twice from acetic acid, melted at 240° (Found : C, 64·9; H, 6·4. $C_{15}H_{18}O_3N_2$ requires C, 65·6; H, 6·6%). It was reprecipitated unchanged from sodium hydroxide solution by hydrochloric acid, and did not decompose sodium hydrogen carbonate. Like the corresponding condensation product of Balbiano's acid, it turned blue litmus violet-red.

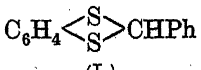
One of us (C. W. S.) desires to thank the Commissioners of the 1851 Exhibition for a Senior Studentship, and the Royal Society for a grant towards the expenses of this investigation.

THE UNIVERSITY, LEEDS. [*Received, January 20th*, 1927.]

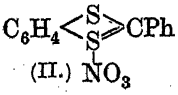
LXXIX.—*Derivatives of* 2-*Phenyl*-1 : 3-*benzdithiole*.

By WILLIAM ROBERT HARDY HURTLEY and SAMUEL SMILES.

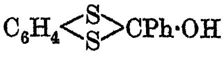
IN a previous communication (J., 1926, 1822), it was shown that 2-phenyl-1 : 3-benzdithiole (I) may be oxidised by nitric acid to the sulphonium nitrate (II), from which the pseudo-base (III) is liberated by alkali. Further experiments on the formation of these sulphonium nitrates have now been made, chiefly with the object of determining whether the process may be generally applied to other members of this group and whether it is subject to the influence of substituents in the 2-phenyl nucleus. The results are summarised as follows.


$C_6H_4{<}\substack{S\\S}{>}CHPh$

(I.)


$C_6H_4{<}\substack{S\\S}{>}CPh$ (NO_3 on S)

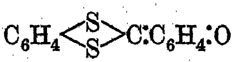
(II.)

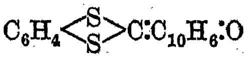

$C_6H_4{<}\substack{S\\S}{>}CPh{\cdot}OH$

(III.)

The presence of a nitro-group in the 2-phenyl nucleus is unfavourable to the formation of the sulphonium salt by oxidation; *e.g.*, the *o*-nitrophenyl derivative (type I) is not attacked by the usual agents. On the other hand, methoxy- and hydroxy-groups facilitate the process. The *nitrate* of the 2-*p*-methoxyphenyl derivative (type II) is very easily formed from the mercaptol (type I), whilst the corresponding *pseudo-base* (type III), which has been characterised as the *oxide* (compare *loc. cit.*, p. 1827), yields more stable salts than the unsubstituted derivative. Oxidation of the *p*- and *o*-hydroxy-derivatives proceeds so easily that unless precautions are adopted it ensues during the formation of the mercaptol (type I) from the hydroxy-aldehyde and *o*-dithiolbenzene. Attempts to obtain the pseudo-base from the salts of 2-*p*-hydroxyphenylbenzdithiole sulphonium (type II) were unsuccessful, since this substance (type III) at the moment of liberation loses the elements of water and is converted into the scarlet *quinone* (IV). A derivative (V) of this interesting type is formed in a similar manner from 2′-hydroxy-2-naphthyl-1 : 3-benzdithiole. Oxidation of this naphthyl derivative takes place so readily that it has not been possible to isolate the mercaptol (type I), the product from *o*-dithiolbenzene and 2-naphtholaldehyde in presence of hydrogen chloride being the chloride of the pseudo-base, which with alkaline media yields the unimolecular *quinone* (V). These quinonoid derivatives yield hydrochlorides which at present are assumed to be of the sulphonium type (II).

(IV.)


$C_6H_4{<}\substack{S\\S}{>}C{:}C_6H_4{:}O$


$C_6H_4{<}\substack{S\\S}{>}C{:}C_{10}H_6{:}O$

(V.)

EXPERIMENTAL.

2-*o*-Nitrophenyl-1 : 3-benzdithiole was obtained by saturating a cooled solution of the dithiol (0·5 g.) and *o*-nitrobenzaldehyde (0·6 g.) in alcohol (15 c.c.) with hydrogen chloride in presence of zinc chloride. The substance (m. p. 106°. Compare Guha and Chakladar, *J. Indian Chem. Soc.*, 1925, 2, 3) was not attacked by cold nitric acid (*d* 1·4) but was destroyed by the boiling reagent. It gave a yellow bromine derivative.

2-p-*Methoxyphenyl*-1 : 3-*benzdithiole* was obtained in almost theoretical yield by treating a solution of the dithiol (1 g.) and anisaldehyde (1 g.) in alcohol (10 c.c.) at 0° with hydrogen chloride for 15 minutes. The liquid product was kept until it had solidified, and after purification from alcohol it melted at 72° (Found : C, 64·6; H, 4·9. $C_{14}H_{12}OS_2$ requires C, 64·6; H, 4·6%). When a warm (not above 40°) solution of this substance in nitric acid (*d* 1·4) was cooled, the *nitrate* of the base (type II) separated in red needles (Found : HNO_3, 32·9. $C_{14}H_{11}OS_2{\cdot}NO_3,2HNO_3$ requires HNO_3, 32·6%). The base (type III) was liberated from this salt by ice-cold 2*N*-aqueous sodium hydroxide and after being dried it was purified from benzene–light petroleum, 2-p-*methoxyphenyl*-1 : 3-*benzdithiole* 2-*oxide* being obtained in colourless prisms, m. p. 158° (Found : C, 62·7; H, 4·5; *M*, 530. $C_{28}H_{22}O_3S_4$ requires C, 62·9; H, 4·1%; *M*, 538). When an acetone solution of this oxide was mixed with concentrated hydrochloric acid, the *chloride* separated in yellow needles [Found : HCl, 18·7. $(C_{14}H_{11}OClS_2)_3,2HCl$ requires HCl, 19·1%].

2-p-*Hydroxyphenyl*-1 : 3-*benzdithiole* (type I) was prepared as in the case of the *p*-methoxy-derivative, but being more soluble, it was isolated by the addition of ice to the reaction mixture. The purification of the product required care owing to the ease with which it is oxidised. The substance was obtained in needles, m. p. 118°, which persistently retained a faint pink tinge (Found : C, 63·3; H, 4·4. $C_{13}H_{10}OS_2$ requires C, 63·4; H, 4·1%). Oxidation of the mercaptol was conducted by trituration with cooled nitric acid; the *nitrate* was then obtained in orange needles [Found : HNO_3, 11·7. $(C_{13}H_9OS_2)_2,HNO_3$ requires HNO_3, 11·4%].

1 : 3-*Benzdithiole*-2-p-*benzoquinone* (IV) was obtained by treating the foregoing nitrate with aqueous potassium carbonate. It was sparingly soluble in warm benzene, from which it separated in scarlet leaflets, m. p. 212—213° (Found : C, 63·9; H, 3·5. $C_{13}H_8OS_2$ requires C, 63·9; H, 3·5%). The substance was easily reduced by a solution of sulphur dioxide in alcohol and yielded a colourless additive product when treated with aqueous sodium bisulphite. The orange *hydrochloride* was obtained from an acetone solution of this substance (Found : HCl, 13·2. $C_{13}H_9OClS_2$ requires HCl, 13·0%).

1 : 3-*Benzdithiole*-2-β-*naphthaquinone* (V).—The normal mercaptol (type I) could not be obtained by interaction of the dithiol and 2-naphthol-1-aldehyde; instead, the oxidation product was isolated as the hydrochloride (II). A cooled solution of the dithiol (2 g.) and the aldehyde (2 g.) in ether (40 c.c.) was treated with hydrogen chloride and kept for 12 hours. On treatment with aqueous

sodium hydroxide the brown impure salt yielded the desired material (2·4 g.). This separated from acetone in small, red needles, m. p. 165° (Found: C, 69·1; H, 3·5; *M*, 293. $C_{17}H_{10}OS_2$ requires C, 69·4; H, 3·4%; *M*, 294). The substance yielded a colourless additive product with sodium bisulphite, but it was not reduced by an alcoholic solution of sulphur dioxide. The *chloride* was obtained in the usual manner and formed red needles (Found: HCl, 11·2. $C_{17}H_{11}OClS_2$ requires HCl, 11·1%).

2-Styryl-1 : 3-benzdithiole, obtained from cinnamaldehyde and the dithiol in the usual manner, formed needles, m. p. 80° (Found: C, 70·2; H, 5·1. $C_{15}H_{12}S_2$ requires C, 70·3; H, 4·7%). When this mercaptol was treated with concentrated nitric acid at 0° for 15 minutes, the *nitrate* of the base (type II) was obtained in orange needles of complex composition [Found: HNO_3, 25·0. $(C_{15}H_{11}S_2{\cdot}NO_3)_4,HNO_3$ requires HNO_3, 24·8%]. The base liberated from this nitrate by alkaline media was too unstable for isolation in the pure condition.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, January 26th,* 1927.]

LXXX.—*The Optical Resolution of Chloroiodoacetic Acid.*

By ANN MORTIMER MCMATH and JOHN READ.

As a result of a study of certain simple compounds with asymmetric molecules containing one and two carbon atoms, we recently came to the conclusion that the optical stability of such molecules was increased in the series under consideration by the substitution of (*a*) SO_3H for CO_2H, and (*b*) I for Br (J., 1926, 2185). We were thus led to anticipate that chloroiodoacetic acid and bromoiodoacetic acid would exhibit a tendency towards racemisation greater than that of chloroiodomethanesulphonic acid, and possibly of the same general order as that shown by chlorosulphoacetic acid. This anticipation has now been substantiated by the preparation and examination of the two optically active modifications of chloroiodoacetic acid, and it is hoped ultimately to secure corresponding evidence for bromoiodoacetic acid.

Chloroiodoacetic acid, which has been rendered readily available through the introduction of the valuable method of Crompton and Carter (J., 1923, **123**, 576), may be resolved with ease into its optically active components, either by fractional crystallisation of the hydroxyhydrindamine salts or by fractional precipitation from aqueous solution with brucine.* With both of these bases the less soluble salt is of the type *l*B*l*A, and in practice the use of *d*-hydroxyhydrindamine would be necessary in preparing the optically pure *d*-acid in quantity through the intermediary of this base. Exceptionally, it has proved possible with the aid of brucine alone to prepare, not only the pure *l*-acid, but also the *d*-acid of practically the same rotatory power, by fractional precipitation from aqueous solutions of different concentrations. The highest optical rotatory powers observed in dilute aqueous solution for ammonium *l*- and *d*-chloroiodoacetate are $[M]_D - 60°$ and $+ 56°$, respectively.

The optical stability of ammonium *d*- and *l*-chloroiodoacetate in aqueous solution appears to be somewhat more pronounced than that of the corresponding derivatives of chlorosulphoacetic acid; a further indication is thus afforded of the stabilising influence of the iodine atom, to which we have drawn attention in preceding communications. The decline in optical rotatory power upon heating such solutions is distinct but not rapid; it is accelerated considerably by the addition of free alkali, and the presence of an equivalent of sodium hydroxide produces complete racemisation at the ordinary temperature in a few hours.

In a recent brief paper, Backer and Mook (*Verslag Akad. Wetenschappen Amsterdam*, 1926, **35**, 737) claim to have obtained aqueous solutions of ammonium *d*- and *l*-chlorobromoacetate displaying a feeble optical activity, the maximum value of $[M]_D$ being $\pm 8°$. We have been unable to establish any such optical activity after repeated fractional separation of the brucine salt from cold water or from alcohol (compare also J., 1926, 2183); moreover, since it is reported that an aqueous solution of the slightly active ammonium chlorobromoacetate containing an equivalent of sodium hydroxide failed to racemise in 24 hours, the optical stability of chlorobromoacetic acid would appear to be even greater than that of chloroiodoacetic acid, a conclusion which is opposed to our current views.

EXPERIMENTAL.

Preparation of Chloroiodoacetic Acid.—The acid was made by the method of Crompton and Carter (J., 1923, **123**, 576), with the following modifications. Upon keeping the mixture of iodine monochloride and αβ-dichlorovinyl ethyl ether for 3 weeks (*loc. cit.*), iodine was often liberated to such an extent that very little chloroiodoacetyl chloride remained. Excellent yields were obtained, however, on warming the reaction mixture to 50° after keeping it for 30 minutes only. Upon then removing the solid iodine by filtration and treating the crude chloroiodoacetyl chloride with the calculated amount of water, hydrolysis was found to be complete within about 4 hours, as indicated by solidification. The yield of the acid was finally enhanced by washing the crude product forthwith with light petroleum, prior to recrystallising the almost colourless residue from this solvent.

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* In presenting these results for publication we acknowledge our indebtedness to Professor Holland Crompton, through whose courtesy we were enabled to inaugurate the experiments concerned, subsequent to the preparation by him of optically active specimens of ammonium chloroiodoacetate.

Following the preparation of chlorobromoacetic acid from chlorobromomalonic acid (J., 1926, 2183), several unsuccessful attempts were made to prepare chloroiodoacetic acid from halogenated malonic or acetic acids, or their esters, by treatment with sodium or potassium iodide in presence of alcohol, ether, or acetone (compare *Ber.*, 1893, **26**, 596; 1910, **43**, 1528). Direct iodination in aqueous or alcoholic solution also proved to be impracticable. Attempts to chlorinate or brominate iodoacetic acid, using sulphuryl chloride and bromine, respectively, in presence of dry ether, likewise resulted in the liberation of iodine. Incidentally, it was not found possible to prepare iodoacetic acid satisfactorily in accordance with the accepted method of heating monochloroacetic acid with potassium iodide in presence of absolute alcohol (compare Sudborough and James, "Practical Organic Chemistry," 1915, p. 118). The yield of the purified acid was increased sevenfold by using acetone in place of alcohol; moreover, the irritating vapour produced in the first method appears to consist mainly of ethyl iodoacetate.

Resolution of Chloroiodoacetic Acid with l-*Hydroxyhydrindamine.*—Hot methyl-alcoholic solutions of the acid (10 g. in 200 c.c.) and base (6·7 g. in 200 c.c.) were mixed in a shallow dish and evaporated to dryness at once, whilst cooling, in a brisk current of air. The residual mass of almost colourless, silky needles was redissolved in the minimum quantity of hot methyl alcohol, diluted considerably with ethyl acetate, and rapidly concentrated on the water-bath until crystallisation occurred readily when the solution was cooled and stirred. Two successive fractions had $[\alpha]_D$ − 32·4° in aqueous solution ($c = 1{\cdot}00$). Upon recrystallisation from the same solvent, separation occurred more readily than from the original solution, and a constant value of $[\alpha]_D$ − 34·0°, $[M]_D$ − 126°, was readily attained for pure l-*hydroxyhydrindamine* l-*chloroiodoacetate* in dilute aqueous solution ($c = 1{\cdot}00$). The salt forms brittle transparent prisms, m. p. 149° (decomp.); it dissolves readily in water or in warm methyl alcohol, sparingly in acetone, and is practically insoluble in ethyl acetate or chloroform (Found: Cl + I, 43·6. $C_{11}H_{13}O_3NClI$ requires Cl + I, 44·0%). The solutions in organic solvents darken when kept. Aqueous solutions exhibited no mutarotation, and only a very slight decrease in rotatory power was observed after evaporating such solutions to dryness. A distinct downward mutarotation occurred in methyl-alcoholic solution ($c = 1·20$), the value of $[M]_D$ declining from $-135°$ to $-103°$ in 5 days; at the same time, the solution gradually developed a brown colour, indicative of decomposition. A solution in glacial acetic acid decomposed much more rapidly, with liberation of iodine. In chloroform containing a little methyl alcohol, the salt gave $[\alpha]_D - 32·0°$, $[M]_D - 118°$ ($c = 0·67$). Upon treatment with the requisite quantity of brucine acetate in hot methyl alcohol, it yielded brucine *l*-chloroiodoacetate, having $[\alpha]_D - 22·0°$ in methyl alcohol ($c = 0·60$); when this salt was decomposed in the cold with ammonia, the resulting ammonium *l*-chloroiodoacetate had $[\alpha]_D - 24·4°$, $[M]_D - 58°$ in aqueous solution ($c = 2·75$).

The mother-liquor from the original separation of *l*-hydroxyhydrindamine *l*-chloroiodoacetate became very dark; after most of the solvent had evaporated, the residual oily mass was induced to crystallise by treatment with light petroleum. Further treatment with ether yielded two fractions, having $[\alpha]_D - 5·9°$ and $-2·0°$, and $[M]_D - 22°$ and $-7°$, respectively, in aqueous solution ($c = 1·00$). The second fraction, composed of minute, feathery needles, appeared to consist of almost pure l-*hydroxyhydrindamine* d-*chloroiodoacetate*, the calculated value for the molecular rotation of the corresponding acid ion in dilute aqueous solution being $+ 53·5°$. The brucine salt precipitated from the mixed fractions was fractionally recrystallised from hot water, and the final fraction, having $[\alpha]_D + 14·0°$ in methyl alcohol ($c = 0·60$), when decomposed in the usual way with dilute ammonia yielded an optically impure ammonium *d*-chloroiodoacetate having $[\alpha]_D + 16·0°$, $[M]_D + 38°$ in aqueous solution ($c = 2·00$).

Resolution of dl-*Chloroiodoacetic Acid with Brucine.*—1. The crude brucine salt, obtained by mixing the components in warm methyl alcohol, had $[\alpha]_D - 9·7°$ in methyl alcohol ($c = 0·60$). Recrystallisation from warm methyl alcohol gave two successive fractions yielding specimens of ammonium chloroiodoacetate with $[\alpha]_D - 2°$ and $+ 1°$, respectively, in dilute aqueous solution.

2. Following preliminary experiments on fractional precipitation with brucine in accordance with the method of Pope and Read (J., 1914, **105**, 817), a warm aqueous solution of ammonium *dl*-chloroiodoacetate (4·4 g. of acid in 300 c.c.) was treated with a

similar solution of one-quarter the calculated weight of brucine hydrochloride (2·3 g. of base in 75 c.c.). After the crystalline brucine salt had been separated from the cold liquid, the filtrate was treated thrice in succession in an exactly similar way with fresh quantities of brucine, the volume of the solution being kept practically constant by evaporation on the water-bath after each filtration. The four fractions of brucine salt had roughly the same weight (2·75 g.), and the respective values of $[\alpha]_D$ in methyl alcohol ($c = 0{\cdot}60$) were − 22°, − 8°, + 6°, and + 8°. After two recrystallisations from water containing a little methyl alcohol, the first fraction gave, upon decomposition with ammonia, a specimen of ammonium *l*-chloroiodoacetate having $[\alpha]_D$ − 25·1°, $[M]_D$ − 60°, in water ($c = 2{\cdot}11$). Further observations indicated that this specimen of ammonium *l*-chloroiodoacetate was optically pure. An aqueous solution of ammonium *l*-chloroiodoacetate (6·53 g. in 250 c.c.) having $[M]_D$ − 32°, prepared from a number of intermediate fractions of the brucine salt which had accumulated in several series of operations, was treated in the usual way with two successive quantities of one-quarter the calculated amount of brucine hydrochloride. The two specimens of ammonium *l*-chloroiodoacetate obtained by decomposing the ensuing fractions of brucine *l*-chloroiodoacetate had the respective values $[\alpha]_D$ − 25·0°, $[M]_D$ − 59°, and $[\alpha]_D$ − 24·4°, $[M]_D$ − 58° in 3% aqueous solution. The two specimens were then mixed and treated once again with one-quarter the calculated amount of brucine hydrochloride under the usual conditions: the resulting brucine salt, when decomposed in the cold with dilute ammonia, yielded ammonium *l*-chloroiodoacetate having $[\alpha]_D$ − 25·0°, $[M]_D$ − 59°. The corresponding pure, air-dried *brucine* l-*chloroiodoacetate* had $[\alpha]_D$ − 22·0° in methyl alcohol ($c = 0{\cdot}60$); this salt forms small, glistening prisms, m. p. 158—160° (decomp.), which dissolve very sparingly in hot water and readily in warm methyl alcohol.

After the addition of one-half the calculated amount of brucine hydrochloride to a hot aqueous solution of ammonium *dl*-chloroiodoacetate, the succeeding fractions of the brucine salt usually exhibit a low dextrorotation in methyl alcohol; the fractions are also more readily soluble and consist of large, glistening prisms. A fraction of the brucine salt having $[\alpha]_D$ + 6° in methyl alcohol yielded ammonium *d*-chloroiodoacetate having $[\alpha]_D$ + 17·5°, $[M]_D$ + 42°, in 4% aqueous solution. After the original brucine salt had been recrystallised three times from hot water, the corresponding ammonium *d*-chloroiodoacetate had $[\alpha]_D$ + 15·0°, $[M]_D$ + 36°. Fractional precipitation of this salt with one-half the calculated quantity of brucine gave an ammonium salt having

$[\alpha]_D$ + 15·8°, $[M]_D$ + 38°. Prolonged evaporation of aqueous solutions of brucine *d*-chloroiodoacetate on the water-bath appears to bring about partial racemisation of the acid component of the salt.

3. The preparation of optically pure brucine *d*-chloroiodoacetate by the normal methods of fractional crystallisation or fractional precipitation is thus difficult; success was achieved, however, by conducting the second of these operations from a solution having about 3·5 times the concentration noted in paragraph (2) above. Two aqueous solutions were prepared, each of 500 c.c.; these contained, respectively, 22·0 g. of *dl*-chloroiodoacetic acid as ammonium salt and 46·6 g. of brucine in the form of hydrochloride. Upon rapidly adding a portion (150 c.c.) of the hot brucine solution to the whole of the first solution on the water-bath, crystallisation began about one minute after mixing and continued rapidly. The fraction (19·8 g.) collected by filtering the cold mixture consisted of practically pure *brucine* d-*chloroiodoacetate*. This had $[\alpha]_D$ + 21·0° in methyl alcohol ($c = 0{\cdot}60$); 0·7647 g. of the corresponding ammonium *d*-chloroiodoacetate contained in 20·0 c.c. of aqueous solution gave α_D + 1·80° in a 2-dcm. tube, whence $[\alpha]_D$ + 23·5° and $[M]_D$ + 56°. A second fraction of brucine salt, yielded similarly by the filtrate from the first fraction, gave a specimen of ammonium *l*-chloroiodoacetate having $[M]_D$ − 32°. Both these fractions of brucine salt were allowed to separate spontaneously without inoculation. Further experiments indicated that the character of the crystalline separation may be controlled to some extent by seeding the supersaturated solution in such instances with specimens of brucine *l*- or *d*-chloroiodoacetate; it is proposed to submit this interesting aspect of the investigation to fuller inquiry.

Ammonium l- *and* d-*Chloroiodoacetate*.—The ammonium salts were prepared by shaking cold aqueous suspensions of the corresponding brucine salts with the calculated amounts of a standard solution of ammonia in presence of chloroform, the ammonia being added in small portions. Traces of brucine were finally removed from the aqueous layer by two further extractions with chloroform. After the value of α_D in a 2-dcm. tube had been observed for the resulting aqueous solution of the ammonium salt, an aliquot portion of the solution was evaporated to dryness on the water-bath in order to determine the concentration. The highest values observed for ammonium *l*- and *d*-chloroiodoacetate were $[\alpha]_D$ − 25·1°, $[M]_D$ − 60°, and $[\alpha]_D$ + 23·5°, $[M]_D$ + 56°, respectively, in dilute aqueous solution as recorded above. The salts form colourless, glistening needles (decomp. 149—150°), which usually become yellow and then brown when kept for a few days in a desiccator (Found : NH_3, 7·2.

$C_2H_5O_2NClI$ requires NH_3, 7·2%). It is thus advisable to keep the active acids in the form of their brucine salts. Crystalline ammonium *l*-chloroiodoacetate having $[\alpha]_D - 25{\cdot}1°$, $[M]_D - 60°$, after being kept for 10 days in a desiccator, gave $[\alpha]_D - 24{\cdot}6°$, $[M]_D - 58°$ in aqueous solution ($c = 0{\cdot}50$) and $[\alpha]_D - 24{\cdot}4°$, $[M]_D - 57°$ in methyl alcohol ($c = 0{\cdot}75$).

No appreciable racemisation was noticed upon evaporating 5 c.c. of a 3·76% aqueous solution of ammonium *d*-chloroiodoacetate, having $[\alpha]_D + 19{\cdot}0°$, to dryness on the water-bath. Sustained evaporation of larger volumes, however, produced a noticeable decline in the rotatory power; a slow decline occurred also on keeping aqueous solutions at the ordinary temperature for long periods.

Upon dissolving 0·2116 g. of ammonium salt having $[M]_D - 58°$ in 20·0 c.c. of water containing 2 c.c. of 2*N*-ammonia and evaporating the solution to dryness on the water-bath, the recovered salt had $[\alpha]_D - 10{\cdot}4°$, $[M]_D - 25°$. Further, 0·2200 g. of ammonium salt having $[\alpha]_D - 24{\cdot}1°$ was dissolved in water containing an equivalent of sodium hydroxide and made up to 20·0 c.c.; the value of α_D in a 2-dcm. tube after 30 minutes was $- 0{\cdot}50°$, and when kept for 24 hours at the ordinary temperature the solution had become optically inactive. No appreciable removal of halogen by hydrolysis was detected at the end of this time. In a similar experiment the value of α_D declined over-night from $- 0{\cdot}68°$ to zero.

An aqueous solution of 0·1882 g. of ammonium salt having $[\alpha]_D + 19{\cdot}0°$, $[M]_D + 44°$, was made up to 20·0 c.c. with water containing one equivalent of hydrochloric acid. The resulting value of α_D in a 2-dcm. tube was $+ 0{\cdot}15°$, whence the free acid under these conditions has $[\alpha]_D + 0{\cdot}9°$, $[M]_D + 2°$.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant and to the Carnegie Trust for a Fellowship which enabled one of them (A. M. M.) to take part in this work. The investigations are being continued.

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UNIVERSITY OF ST. ANDREWS. [*Received, January 7th,* 1927.]

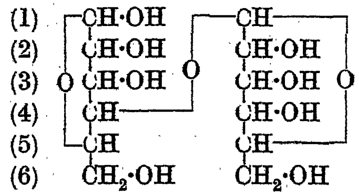
LXXXI.—*The Constitution of the Disaccharides. Part XII. Lactose.*

By WALTER NORMAN HAWORTH and CHARLES WILLIAM LONG.

THE constitutional study of lactose (Haworth and Leitch, J., 1918, **113**, 188) showed that from completely methylated lactose the products of hydrolytic cleavage were crystalline 2 : 3 : 6-trimethyl glucose and normal tetramethyl galactose, and a structural formula was applied to lactose on this experimental basis. These results have since been experimentally verified by Irvine and Hirst (J., 1922, **121**, 1213) and by Schlubach and Moog (*Ber.*, 1923, **56**, 1957).

In the subsequent communication in which the evidence for a complete revision of the structure of normal glucose was outlined—a revision which extended also to all carbohydrates containing glucose residues—it was shown that derivatives of normal glucose should be represented by an amylene-oxide ring structure (Charlton, Haworth, and Peat, J., 1926, 89). In the latter paper, therefore, the constitutional formula previously applied to lactose and cellobiose was revised by the introduction of the above emendation. This involved the change from a butylene-oxide structure to the new amylene-oxide formulation in each of the hexose residues, and also a corresponding adjustment in the point of attachment of the biose linking from position 5 to position 4.

(I.)

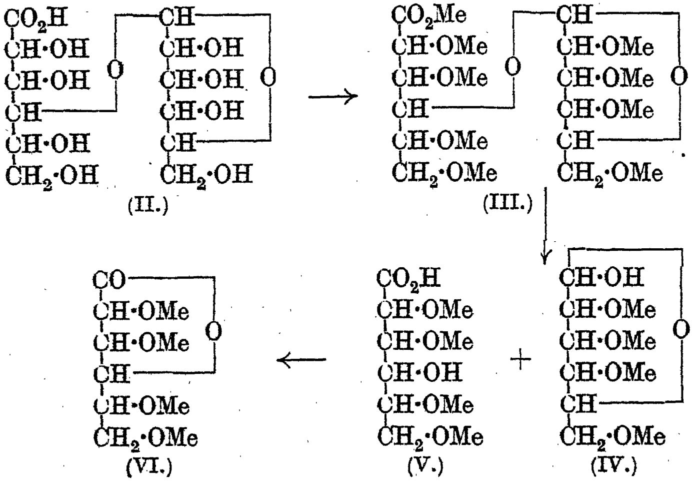


Glucose residue. Galactose residue.

At the same time, it was recognised that the isolation of 2 : 3 : 6-trimethyl glucose as a cleavage fragment of methylated lactose left open the unlikely contingency of the presence of a butylene-oxide ring or γ-sugar residue in the reducing half of the disaccharide, since the positions 4 and 5 were available either for the allocation of an oxide-ring attachment or for the position of the biose linking. The reason for suspending final judgment in regard to this contingency was fully explained. It was pointed out that crystalline 2 : 3 : 6-trimethyl glucose, although itself an amylene-oxide sugar, could conceivably have originated as a labile butylene-oxide form at the moment of its separation from methylated lactose, and had thereafter undergone isomeric change into the normal amylene-oxide variety which was isolated. It was recognised, however, that lactose did not itself display the behaviour of a labile or γ-sugar, and consequently we preferred the structural formula (I) which was definitely advanced.

In a subsequent paper, Irvine and Black (J., 1926, 862) took occasion to criticise the formulæ we had applied to the reducing disaccharides, including lactose and cellobiose, the constitutions of which they regarded as conjectural. Following this criticism, two papers have since appeared (G. Zemplén, *Ber.*, 1926, **59**, 1254, 2402) describing the constitutional study of lactose and cellobiose by degradation to the hexose-tetroses, and the experimental results entirely confirm the structural formulæ we had applied to lactose and cellobiose. Inasmuch as exception might be taken, however, to the method of Zemplén, whose proof depends upon the non-formation of phenylosazones by the hexose-tetroses, we have continued our work on the constitutional study of lactose, and have adopted a scheme, herein described, which furnishes, in our view, quite definite proof of the position occupied by the biose linking in this disaccharide; and consequently the nature of the oxide ring also is fully established.

In this experimental work, we oxidised lactose to lactobionic acid, the barium salt of which was methylated, thus giving rise to methyl octamethyl-lactobionate. In this compound it will be seen that the oxide-ring in the reducing hexose residue of the parent disaccharide has been eliminated, and the hydroxyl position thus exposed has been protected by a methyl residue, whilst the biose linking has presumably remained intact. Hydrolysis of this methylated lactobionate should give cleavage products which leave no doubt as to the position of the biose linking, since only one free hydroxyl group would be exposed in the hexonic acid residue resulting from the hydrolysis. On digesting the methyl octamethyl-lactobionate with dilute hydrochloric acid, we were able to isolate crystalline 2 : 3 : 4 : 6-tetramethyl galactose (IV), which had already been recognised in the course of previous work, and also crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone (VI), identical in every respect with the specimen we had recently isolated in the course of a similar investigation on maltose (Haworth and Peat, J., 1926, 3094). This crystalline lactone gave rise to a crystalline phenylhydrazide of the corresponding 2 : 3 : 5 : 6-tetramethyl gluconic acid (V), and consequently the diagnosis of these two products arising from the cleavage of the methylated lactobionic acid enables us to ascribe a constitutional formula (III) to methyl octamethyl-lactobionate and the formula (II) to lactobionic acid. It therefore follows that the constitution (I) which we had already advanced and supported in the course of our earlier work receives further experimental verification.



EXPERIMENTAL.

Methylation of Lactobionic Acid. Isolation of Methyl Octamethyllactobionate.—Lactobionic acid was prepared by the oxidation of lactose with bromine water, and the procedure described by Fischer and Meyer (*Ber.*, 1889, **22**, 1941) was adopted as a means of obtaining the calcium and the barium salt. An aqueous solution of the latter salt was gradually added to a large volume of alcohol which was well stirred. Barium lactobionate was precipitated as a colourless, micro-crystalline solid which contained 14·0% of barium. Calcium lactobionate, purified by the same method, contained 4·6% of calcium. It would thus appear that each salt is associated with three molecules of ethyl alcohol, and this seems to be true also of calcium maltobionate. The salts were neutral and devoid of action towards Fehling's solution.

Barium lactobionate was methylated in a manner similar to that already mentioned in the case of calcium maltobionate (Haworth and Peat, *loc. cit.*). After eight treatments with the methylating agents, a preliminary distillation at 0·09 mm. pressure showed little evidence of hydrolytic cleavage. Thus from a total distillate of 16·5 g., only 1·7 g. were collected at a bath temperature of 170—180°, and this first fraction showed $n_D^{13^\circ}$ 1·4561. The main distillate (14·8 g.), a pale yellow, viscid liquid, showed b. p. 178—210°/0·09 mm. and $n_D^{13^\circ}$ 1·4625—1·4689. This was subjected to one methylation with moist silver oxide and methyl iodide, followed by two further treatments with the dry reagents, and at this stage the material was again distilled. A small first fraction (0·5 g.), which distilled at a bath temperature of 160—180° under 0·08 mm. and had $n_D^{13°}$ 1·4612, having been rejected, the main portion was collected at a bath temperature of 180—185° and distilled at 157—164°/0·05 mm. This specimen of methyl octamethyl-lactobionate, which was devoid of action towards Fehling's solution, showed $n_D^{13°}$ 1·4632 (Found: C, 51·8; H, 8·1; OMe, 54·8. Calc. for $C_{21}H_{40}O_{12}$: C, 52·1; H, 8·3; OMe, 57·6%).

Hydrolysis. The above specimen was hydrolysed in contact with 7·0% hydrochloric acid at 80—90° during 6½ hours. Portions of the solution were examined polarimetrically at intervals: $[\alpha]_D$ (initial), + 34·0°; 72·6° (after 1 hour); 74·5° (2 hours); 76·8° (3 hours); 77·6° (4 hours); 77·6° (5½ hours); 77·2° (6½ hours). The hydrolysis was probably complete after 4 hours, and certainly after 6½ hours; no appreciable change had occurred in the appearance of the solution, which now reduced Fehling's solution.

At this stage, the solution was gently heated in contact with barium carbonate until the whole of the acid product was neutralised. The colourless filtrate was evaporated under diminished pressure, and the dried residue was repeatedly extracted with ether until it no longer gave a positive test with Fehling's solution. From this ethereal extract, colourless crystals of tetramethyl galactose were isolated, showing $[\alpha]_D$ + 118·1° in equilibrium in water (yield, 95%). A mixed melting-point determination of this substance with an authentic specimen of crystalline 2 : 3 : 4 : 6-tetramethyl galactose (compare Haworth, Ruell, and Westgarth, J., 1924, **125**, 2473) gave m. p. 71—72°. Schlubach and Moog (*loc. cit.*) gave m. p. 71·5—72° for the sugar they then described as 2 : 3 : 5 : 6-tetramethyl galactose.

The crystalline anilide was prepared (m. p. 190—191°), and this m. p. was not depressed in admixture with an authentic specimen of 2 : 3 : 4 : 6-tetramethyl galactose anilide (Found: C, 61·7; H, 7·9. Calc.: C, 61·7; H, 8·0%).

Separation of 2 : 3 : 5 : 6-Tetramethyl γ-Gluconolactone.—The colourless residue of barium salts was dissolved in the minimum of water and the free organic acid was liberated by the cautious addition of *N*/2-hydrochloric acid. Evaporation at 30°/14 mm., followed by a period of heating at 60°/0·09 mm., gave a dried residue containing barium chloride and the organic lactone, from which the latter was extracted by means of dry ether. Evaporation of the ethereal solution furnished a liquid product which was distilled under 0·03 mm. at a bath temperature of 117—135°. The cooled distillate was nucleated with a specimen of crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone prepared by oxidation of 2 : 3 : 5 : 6-tetramethyl γ-glucose, and thereafter it crystallised completely

(m. p. 26—28°), and a mixture of this substance with an authentic specimen obtained in the course of recent work on the hydrolysis of methyl octamethylmaltobionate (Haworth and Peat, *loc. cit.*) melted at 26—27·5° (yield, 90% of the theoretical).

The phenylhydrazide was prepared as colourless, silky needles, m. p. 136° (remelted at 135—136°). Also the m. p. of a mixture of this specimen with that prepared by Haworth and Peat (*loc. cit.*) from methyl octamethylmaltobionate showed no depression (Found by micro-analysis: C, 56·35; H, 7·6; OMe, 34·1. Calc.: C, 56·1; H, 7·6; OMe, 36·3%).

The authors gratefully acknowledge a maintenance grant to one of them from the Department of Scientific and Industrial Research.

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[*Received, January 22nd*, 1927.]

LXXXII.—*A New Synthesis of Oxyberberine and a Synthesis of Palmatine.**

By ROBERT DOWNS HAWORTH, JOSEPH BLAKE KOEPFLI, and WILLIAM HENRY PERKIN, jun.

THE general method devised for the synthesis of the berberine type of alkaloid (Haworth, Perkin, and Pink, J., 1925, **127**, 1709) has been applied to the synthesis of *epi*berberine and of 2 : 3 : 9 : 10-bismethylenedioxyprotoberberine † by utilising 3 : 4-methylenedioxyhomophthalic acid (Haworth and Perkin, J., 1926, 1769) as the starting point.

The present communication describes the preparation of 3 : 4-*dimethoxyhomophthalic anhydride* (I) and the use of this substance in the synthesis of oxyberberine and palmatine. 3 : 4-Dimethoxyhomophthalic anhydride (I) was prepared by a slight modification of the method used in the preparation of 3 : 4-methylenedioxyhomophthalic acid (Haworth, Perkin, and Stevens, J., 1926, 1764). β-Veratrylpropionic acid was brominated and the β-6-*bromoveratrylpropionic acid* converted into 4-*bromo*-6 : 7-*dimethoxy*-1-*hydrindone* (II) by treatment with concentrated sulphuric acid. The iso*nitroso*-derivative was prepared in the usual manner and treated with toluene-*p*-sulphonyl chloride in alkaline solution, and the resulting 6-*bromo*-2-*carboxy*-3 : 4-*dimethoxyphenylacetonitrile* was hydrolysed to 6-*bromo*-3 : 4-*dimethoxyhomophthalic acid* (III). This acid was debrominated in alkaline solution with sodium amalgam, and the crude 3 : 4-dimethoxyhomophthalic acid converted into its *anhydride* (I) by the action of acetyl chloride.

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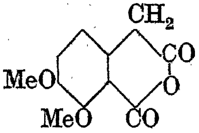
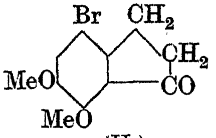
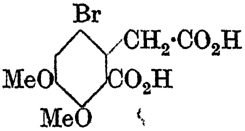
* Compare Späth and Quietensky (*Ber.*, 1925, **58**, 2267).

† Kitasato (*Proc. Imp. Acad. Tokyo*, 1926, **2**, 124) has recently isolated an alkaloid from *Coptis japonica*, which he has named coptisine. This alkaloid appears to be identical with 2 : 3 : 9 : 10-bismethylenedioxyprotoberberine, obtained as an intermediate stage in the synthesis of protopine (Haworth and Perkin, *loc. cit.*, p. 1783).


(I.)

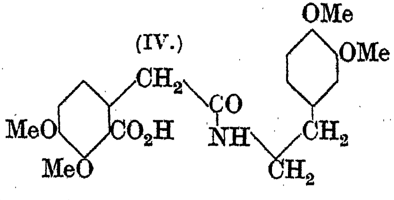

(II.)


(III.)

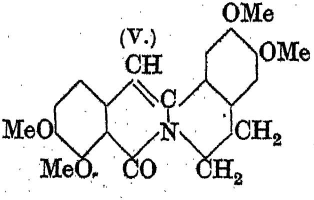
In order to establish the constitution of the anhydride (I), and the possibility of its application to the syntheses of substances of the berberine type, it was first condensed with β-piperonylethylamine, the resulting unpurified amic acid esterified, the crude methyl ester boiled with phosphorus oxychloride, and the resulting oxyberberine identified by comparison with a specimen obtained by the action of sodium hydroxide on berberinium chloride.

For the synthesis of palmatine, 3 : 4-dimethoxyhomophthalic anhydride (I) was condensed with β-veratrylethylamine, and N-β-*veratrylethyl*-3 : 4-*dimethoxyhomophthalamic acid* (IV) was obtained as a gum which so far has not been crystallised. The *methyl* ester, prepared from the silver salt of the acid (IV), was converted by treatment with phosphorus oxychloride into a substance, $C_{21}H_{21}O_5N$, m. p. 183°, which exhibited the properties characteristic of a substance of the oxyberberine type. There can be no doubt that this substance is *oxypalmatine* (V), which does not appear to have been previously described. The oxypalmatine was reduced electrolytically and thus converted into a base, m. p. 147°, which was identical with a specimen of tetrahydropalmatine (VI) obtained by reducing palmatine iodide. The synthetical tetrahydropalmatine was next oxidised by iodine to a bright yellow iodide and this was identical with a specimen of palmatine iodide (VII) obtained from the natural alkaloid.*

(IV.)



(V.)



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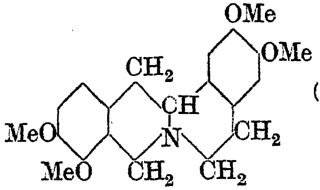
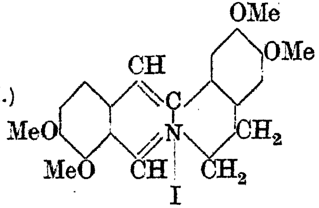
* Professor E. Späth was kind enough to furnish us with a sample of palmatine iodide of natural origin, which made direct comparison possible.

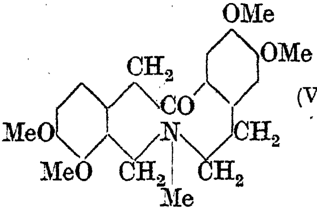
The authors are continuing these researches with a view to the synthesis of the ten-membered ring alkaloid (VIII).



(VI.)

(VII.)





(VIII.)

EXPERIMENTAL.

β-6-*Bromoveratrylpropionic Acid*.—Bromine (1¼ mols.), dissolved in glacial acetic acid (1 part), was gradually added with shaking and cooling to β-veratrylpropionic acid (1 mol.) in glacial acetic acid (2 parts). The bromo-acid rapidly separated, and, after remaining for 12 hours, the mixture was diluted with water and the acid was collected and dried; it recrystallised from benzene in colourless prisms, m. p. 118—119° (yield, 90% of the theoretical) (Found: C, 46·0; H, 4·5. $C_{11}H_{13}O_4Br$ requires C, 45·7; H, 4·5%).

4-*Bromo*-6 : 7-*dimethoxy*-1-*hydrindone* (II).—β-6-Bromoveratrylpropionic acid (10 g.) was dissolved in concentrated sulphuric acid (50 c.c.) at 75°, and maintained at this temperature for 5 minutes. The deep red solution was poured into ice and extracted with chloroform; the extract was washed with aqueous sodium carbonate and dried, and the solvent removed.* The residual oil, which solidified on rubbing, crystallised from methyl alcohol in almost colourless needles (2·5 g.), m. p. 120—121° (Found: C, 48·5; H, 4·0. $C_{11}H_{11}O_3Br$ requires C, 48·7; H, 4·1%). The *oxime*, prepared by the action of hydroxylamine hydrochloride and potassium acetate on an alcoholic solution of the bromohydrindone (II), is sparingly soluble in ethyl alcohol, from which it crystallises in colourless prisms, m. p. 228—230° (Found: N, 4·7. $C_{11}H_{12}O_3NBr$ requires N, 4·8%).

4-*Bromo*-2-iso*nitroso*-6 : 7-*dimethoxy*-1-*hydrindone*.—The bromohydrindone (II) (2 g.), dissolved in the minimum of methyl alcohol containing concentrated hydrochloric acid (3 c.c.), was saturated with methyl nitrite; the precipitated iso*nitroso*-derivative crystallised from ethyl alcohol in slender, elongated, pale yellow prisms (2 g.), m. p. 236° (decomp.) (Found: C, 44·2; H, 3·4. $C_{11}H_{10}O_4NBr$ requires C, 44·0; H, 3·3%).

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* In attempts to prepare the hydrindone (II) on a larger scale, debromination occurred to a considerable extent, resulting in the formation of a mixture of the bromohydrindone (II) and 5 : 6-dimethoxy-1-hydrindone.

6-*Bromo*-2-*carboxy*-3 : 4-*dimethoxyphenylacetonitrile.* — The *iso*nitrosohydrindone (2 g.) in aqueous sodium hydroxide (18 c.c. of 8%) was gradually treated with toluene-*p*-sulphonyl chloride (2 g.) with shaking, and solution completed by raising the temperature to 80°. When the mixture was cooled, filtered, and acidified with hydrochloric acid, the *nitrile* separated as an oil, which solidified on rubbing and crystallised from much boiling water in almost colourless needles, containing $1H_2O$, m. p. 98—100° (Found: loss at 100°, 5·1. Calc. for $1H_2O$, 5·6%. Found in material dried at 100°: C, 43·5; H, 3·6. $C_{11}H_{10}O_4NBr$ requires C, 44·0; H, 3·3%).

6-*Bromo*-3 : 4-*dimethoxyhomophthalic Acid* (III).—Crude 6-bromo-2-carboxy-3 : 4-dimethoxyphenylacetonitrile was boiled with sodium hydroxide solution (8%) until evolution of ammonia had ceased. The solution was acidified with dilute hydrochloric acid, extracted several times with ether and dried, the ether removed, and the residual light brown gum refluxed with a slight excess of acetyl chloride for ½ hour. After evaporation under reduced pressure, the *anhydride* separated, and crystallised from benzene in very pale yellow, glistening plates, m. p. 151° (Found: C, 44·0; H, 3·0. $C_{11}H_9O_5Br$ requires C, 43·9; H, 3·0%). 6-*Bromo*-3 : 4-*dimethoxyhomophthalic acid* (III) was obtained by hydrolysing the above anhydride with sodium hydroxide solution (8%), acidifying the mixture with hydrochloric acid, extracting it with ether, drying the extract and removing most of the solvent, adding benzene, and removing the remaining ether. The acid (III) slowly separated in colourless prisms, m. p. 166—167°, which were readily soluble in water and ether but sparingly soluble in benzene (Found: C, 41·4; H, 3·4. $C_{11}H_{11}O_6Br$ requires C, 41·6; H, 3·5%).

3 : 4-*Dimethoxyhomophthalic Anhydride* (I).—Pure bromodimethoxyhomophthalic anhydride (5 g.) was dissolved in sodium hydroxide solution (8%), diluted with water, and heated on the water-bath for 12 hours with sodium amalgam (150 g. of 4%). The solution was cooled, filtered, acidified, and extracted several times with ether, the extract dried, the ether removed, and the residual brown oil, consisting of 3 : 4-dimethoxyhomophthalic acid, converted into 3 : 4-*dimethoxyhomophthalic anhydride* (I) by boiling with acetyl chloride, which was then evaporated under reduced pressure. The

anhydride separated from dry benzene in almost colourless plates, m. p. 104—105°, which became sticky on long standing owing to absorption of water (Found: C, 59·6; H, 4·5. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%). A crystalline specimen of 3 : 4-dimethoxyhomophthalic acid has not yet been obtained.

Oxyberberine.—A benzene solution of 3 : 4-dimethoxyhomophthalic anhydride (I) (1·1 g.) and β-piperonylethylamine (from 2·0 g. of the hydrochloride) was refluxed for 1 hour, the solution extracted with aqueous sodium hydroxide (8%), the alkaline layer acidified, the precipitated oily amic acid extracted with chloroform and dried, and the solvent removed. The residual gum (1·5 g.) was dissolved in water containing sodium bicarbonate (0·35 g.), and the filtered solution was treated with silver nitrate (1·0 g.). After remaining over-night, the precipitated silver salt was collected, successively washed with water, methyl alcohol, and ether, dried, powdered, suspended in ether, and refluxed for 12 hours with excess of methyl iodide. After filtering from the silver salts, the ether was removed, and the residual gum boiled with phosphorus oxychloride for 5 minutes, forming a red solution. The excess of the oxychloride was removed under reduced pressure, and the residue was diluted with hot water, treated with charcoal, and filtered. The filtrate was made alkaline with sodium hydroxide, the amorphous precipitate extracted with chloroform, the solvent removed from the extract, and the residue digested for some time with dilute hydrochloric acid; the solid obtained crystallised from glacial acetic acid, containing a little water, in pale yellow needles, m. p. 197·5°. After three successive crystallisations from alcohol, xylene, and alcohol, pale yellow needles (0·15 g.), m. p. 198—200°, were obtained, which showed no depression in m. p. when mixed with a specimen of oxyberberine prepared by the action of sodium hydroxide on berberinium chloride. The colour reactions of the synthetical product corresponded with those exhibited by oxyberberine.

N-β-*Veratrylethyl*-3 : 4-*dimethoxyhomophthalamic Acid* (IV).—3 : 4-Dimethoxyhomophthalic anhydride (I) (1·2 g.) and β-veratrylethylamine (1·0 g.) were refluxed for 3 hours in benzene (10 c.c.), and the product was extracted with sodium hydroxide solution (5%), the alkaline layer acidified, the precipitated light brown oil extracted with chloroform, the extract dried, and the solvent removed. The residual oil (2·0 g.) was dissolved in water, containing sodium bicarbonate (0·5 g.), and treated with excess of silver nitrate. After 12 hours, the precipitated silver salt was collected, washed successively with water, methyl alcohol, and ether, dried in a desiccator, powdered, suspended in ether, and refluxed with excess of methyl iodide for 12 hours. After filtering from silver salts, the ethereal solution was concentrated; the crystalline *methyl* ester, m. p. 90—94°, obtained recrystallised from ether in colourless plates, m. p. 93—94° (Found: C, 63·4; H, 6·5. $C_{22}H_{27}O_7N$ requires C, 63·3; H, 6·4%). It is soluble in most organic solvents with the exception of light petroleum.

Oxypalmatine (V).—The methyl ester was boiled with phosphorus oxychloride for 10 minutes, and the dark red solution concentrated under diminished pressure. A solution of the residue in boiling water was treated with charcoal, filtered, and made alkaline with sodium hydroxide, and the precipitate was extracted with chloroform. The extract was dried, the chloroform removed, and the residue digested with dilute hydrochloric acid; the crystalline solid obtained recrystallised from methyl alcohol in buff-coloured prisms, m. p. 183° (Found: C, 68·8; H, 5·6. $C_{21}H_{21}O_5N$ requires C, 68·6; H, 5·7%).

Oxypalmatine dissolves in glacial acetic acid and is precipitated by addition of water, and its solution in ethyl alcohol or benzene exhibits a bluish-violet fluorescence. When it is treated with sulphuric acid (50%), a sparingly soluble, bright yellow *sulphate* separates and the addition of a drop of concentrated nitric acid produces an intense violet coloration.

Tetrahydropalmatine (VI).—Oxypalmatine (1 g.), dissolved in methyl alcohol (60 c.c.) and concentrated sulphuric acid (40 c.c.), was reduced in an electrolytic cell with a current of 4½ amps. for 18 hours with water-cooling and for a further 6 hours without cooling. The almost colourless solution was diluted with an equal volume of water, treated with charcoal, filtered, made alkaline with ammonia, and extracted with chloroform, and the extract was dried and the solvent removed. The residue, consisting of crude tetrahydropalmatine, was converted into the sparingly soluble hydrochloride by the action of a little dilute hydrochloric acid. The hydrochloride was collected, dissolved in hot water, and treated with sodium hydroxide; the amorphous base thus obtained crystallised from methyl alcohol in colourless, rhombic plates, m. p. 147° (Found: C, 71·2; H, 7·1. Calc. for $C_{21}H_{25}O_4N$: C, 71·0; H, 7·0%). A specimen of tetrahydropalmatine was prepared by reducing palmatine iodide with zinc dust and dilute sulphuric acid, and no alteration was observed in the melting point of a mixture of this and the synthetical base.

Palmatine Iodide (VII).—Synthetical tetrahydropalmatine (0·1 g.), dissolved in ethyl alcohol, was oxidised by boiling it with an excess of alcoholic iodine in the presence of potassium acetate. The red periodide which rapidly separated was collected, washed with ethyl alcohol, suspended in much boiling water, and decomposed with sulphurous acid, and the solution obtained was filtered and cooled. The sparingly soluble palmatine iodide separated in long, orange-yellow needles, m. p. 241° (decomp.), and showed no depression in melting point when mixed with a specimen of palmatine iodide sent us by Professor E. Späth.

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[*Received, February 3rd*, 1927.]

LXXXIII.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part II. 1 : 2- and 2 : 3-Thionyldihydroxyanthracenes.*

By ALBERT GREEN.

PHENOLIC thionyl derivatives have been classified (this vol., p. 500) according to their behaviour with weak organic acids. In the present paper, the thionyl derivatives of dihydroxyanthracenes are compared with those of the corresponding dihydroxyanthraquinones (J., 1924, **125**, 1450; 1926, 2198).

1 : 2-Dihydroxyanthracene is obtainable from 1 : 2-dihydroxyanthranol (deoxyalizarin) by Perkin's reduction method (J., 1923, **123**, 2029).

2 : 3-Dihydroxyanthracene has been described, as straw-yellow plates darkening at 180° and melting at about 192°, by Lagodinski (*Annalen*, 1905, **342**, 106), who obtained it by boiling its dimethyl ether with hydriodic acid. The diacetyl derivative melted at 155—160°. The present author prepared 2 : 3-dihydroxyanthracene from hystazarin by the two-stage reduction method (stannous chloride followed by the aluminium-mercury couple) used by Perkin (*loc. cit.*, pp. 2029, 2606) in the preparation of other hydroxyanthracenes from the hydroxyanthraquinones. The properties of the intermediate anthranol so obtained agreed with those ascribed to it by Schrobsdorff (*Ber.*, 1903, **36**, 2938), who reduced hystazarin by means of zinc dust and ammonia. 2 : 3-Dihydroxyanthranol, on reduction by the couple, gave a product, m. p. 282°, whose diacetyl derivative melted at 175°. These properties do not agree with those of Lagodinski's substance, but confirmation of the new product as 2 : 3-dihydroxyanthracene was obtained by analyses, by molecular-weight determinations, and by the oxidation of the acetyl derivative to diacetylhystazarin. The colour reactions of the compound described herein conform substantially with those of Lagodinski's substance, and the probability of the latter having

been obtained in a very impure state is supported by the indefinite melting point and the yellow colour ascribed to the acetyl derivative.

Unfortunately, all attempts to prepare the dimethyl ether from 2 : 3-dihydroxyanthracene were fruitless, although methyl sulphate, diazomethane, and hydrolysis of the diacetyl derivative by sulphuric acid and by hydrogen chloride in absolute methyl-alcoholic solution were resorted to. Similar resistance of other dihydroxyanthracenes to etherification has been noted by Perkin (*loc. cit.*, p. 2035). Lagodinski prepared his 2 : 3-dimethoxyanthracene from veratrole and phthalic anhydride through *o*-3′ : 4′-dimethoxybenzoylbenzoic acid.

1 : 2- and 2 : 3-*Thionyldihydroxyanthracenes* were obtained by the interaction of the hydroxy-compounds and thionyl chloride in pyridine–carbon disulphide solution. They are remarkably stable to moisture, remaining unchanged after 6 weeks' contact with moist air; thionylalizarin (*loc. cit.*) completely reverts to alizarin on standing in air over-night. Both thionyl compounds are decomposed to the dihydroxyanthracenes by solution in cold concentrated sulphuric acid or in cold aqueous caustic alkali.

1 : 2-Thionyldihydroxyanthracene shows no signs of reacting with acetic acid until this boils; complex decomposition then occurs and sulphur and sulphur dioxide are produced. This unexpectedly complex reaction may be accounted for by the proximity of the reaction temperature to the m. p. of the thionyl compound, which darkens at 125° and melts at 138—139° (decomp.). A similar reaction occurs when it is heated with acetic acid and pyridine.

2 : 3-Thionyldihydroxyanthracene differs from thionylhystazarin (*loc. cit.*) in not reacting with boiling acetic acid. When a trace of pyridine is added to the solution, decomposition proceeds slowly with evolution of sulphur dioxide and formation of 2 : 3-dihydroxyanthracene. This "hydroxylic decomposition" corresponds with that of thionylhystazarin. 2 : 3-Thionyldihydroxyanthracene is quantitatively converted into 2 : 3-diacetoxyanthracene by acetic anhydride and pyridine.

EXPERIMENTAL.

1 : 2-*Dihydroxyanthracene.*—The crude reduction product from deoxyalizarin was acetylated, and the purified diacetyl derivative was hydrolysed in small quantities (1 to 2 g.) by means of acetic and hydrochloric acids (Perkin, *loc. cit.*). This tedious process appears to provide the best means of obtaining pure 1 : 2-dihydroxyanthracene in faintly green plates, m. p. 160—161° (Found: C, 79·8; H, 4·9. Calc.: C, 80·0; H, 4·8%).

2 : 3-*Dihydroxyanthracene.*—Hystazarin was recovered practically unchanged after attempts to reduce it directly to 2 : 3-dihydroxyanthracene by the aluminium–mercury couple, alcohol and ammonia.

(a) 2 : 3-*Dihydroxyanthranol.* Finely-divided, moist hystazarin, obtained by hydrolysis of its pure diacetate (compare J., 1926, 2199) with sulphuric acid, when boiled with a hydrochloric acid solution of stannous chloride until a test portion, dissolved in excess of caustic soda, showed a light greenish-yellow colour, gave a quantitative yield of the anthranol, which crystallised from alcohol in bunches of small, yellowish-brown rods, m. p. 288—289° (Schrobsdorff, *loc. cit.*, gives m. p. 282°) (Found : C, 74·2; H, 4·4. Calc. : C, 74·3; H, 4·4%). Its aqueous and alcoholic solutions give an olive-green colour with ferric chloride, and the other colour reactions correspond with those described by Schrobsdorff.

The triacetyl derivative, prepared by means of acetic anhydride and pyridine, formed white, hair-like needles (from alcohol), m. p. 164° (Found : $CH_3·CO$, 36·8. Calc. : $CH_3·CO$, 36·6%).

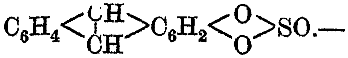
(b) 2 : 3-*Dihydroxyanthracene.* The crude damp anthranol was suspended in a mixture of water and alcohol and reduced by the aluminium–mercury couple. No tar formed, and when the mixture was stirred into dilute hydrochloric acid the hydroxyanthracene was precipitated, in theoretical yield, as a pale buff solid.

2 : 3-*Diacetoxyanthracene* was prepared by boiling this solid with acetic anhydride and pyridine; after one recrystallisation from rectified spirit, it formed white, elongated, hexagonal plates of constant m. p. 175° [Found : C, 73·4; H, 4·8; $CH_3·CO$, 29·5; *M*, cryoscopic in naphthalene, 286, 290. $C_{14}H_8O_2(CO·CH_3)_2$ requires C, 73·5; H, 4·8; $CH_3·CO$, 29·3%; *M*, 294].

2 : 3-*Dihydroxyanthracene* was obtained pure by hydrolysing the acetyl derivative with a mixture of acetic and hydrochloric acids. It separated as faintly greenish-yellow plates, which began to sublime at about 260° and melted at 282° (Found : C, 79·9; H, 4·8; *M*, cryoscopic in naphthalene, 212, 204. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%; *M*, 210).

2 : 3-Dihydroxyanthracene dissolves in concentrated sulphuric acid with a bright golden-brown colour, and in aqueous caustic soda and in ammonia to pale green solutions. Its solutions in alcohol and in acetone are very light yellow and show a faint purple fluorescence; addition of ferric chloride to these produces a dark bluish-green colour.

(c) *Oxidation of* 2 : 3-*diacetoxyanthracene.* A boiling solution of 1 g. of 2 : 3-diacetoxyanthracene in 8 c.c. of glacial acetic acid was carefully treated with 1·6 g. of chromic anhydride dissolved in a mixture of 1·5 c.c. of water and 3 c.c. of acetic acid. After boiling for 10 minutes, the solution was stirred into water. The precipitate, after drying at 100° (1·1 g.), melted at 206—209°, and, after recrystallisation from pyridine, at 211—213°, either alone or when mixed with authentic diacetylhystazarin (Found : C, 66·5; H, 3·7; $CH_3\cdot CO$, 26·4. Calc. : C, 66·7; H, 3·7; $CH_3\cdot CO$, 26·6%).

1 : 2-*Thionyldihydroxyanthracene*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{CH}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}SO$.—An excess of cold thionyl chloride reacted very vigorously with 1 : 2-dihydroxyanthracene, but the product did not yield the required thionyl derivative. This was obtained by adding 2·10 c.c. (1 mol.) of freshly-distilled thionyl chloride in 30 c.c. of dry carbon disulphide to a cold solution of 5·85 g. (1 mol.) of 1 : 2-dihydroxyanthracene in a mixture of 4·40 g. (2 mols.) of pyridine and 200 c.c. of dry carbon disulphide. The mixture was boiled on the water-bath for 20 minutes, and the hot disulphide solution was then decanted from the viscous pyridine hydrochloride and concentrated to 50 c.c. The residue in the flask was extracted with a further 200 c.c. of dry carbon disulphide, and this solution also was concentrated. From the two solutions, 4·8 g. of small, pale brown crystals separated. These darkened at about 125° and melted at 138—139° (decomp.) (Found: C, 65·4; H, 3·2; S, 12·6; *M*, cryoscopic in naphthalene, 254, 250. $C_{14}H_8O_3S$ requires C, 65·6; H, 3·1; S, 12·5%; *M*, 256).

1 : 2-*Thionyldihydroxyanthracene* dissolves in cold concentrated sulphuric acid with a transient dark orange colour which rapidly passes to royal-blue; on dilution with water, 2 : 3-dihydroxyanthracene separates. Its solution in cold aqueous caustic soda is light orange-yellow, and when acidified deposits the dihydroxy-compound. The thionyl compound dissolves in cold alcohol to a dark orange solution on which ferric chloride has no apparent effect.

Two finely powdered specimens, after standing in the air for 6 weeks, had their original weights and m. p. and sulphur contents of 12·6 and 12·5%, respectively.

2 : 3-*Thionyldihydroxyanthracene* was obtained in a similar manner to the 1 : 2-compound, 4·50 g. of the dihydroxyanthracene yielding 3·4 g. of the thionyl derivative. This separated from carbon disulphide in thin, faintly yellow flakes, which darkened at 180° and melted at 188° (decomp.) (Found : C, 65·5; H, 3·1; S, 12·6%; *M*, in freezing naphthalene, 260, 264). After standing in air for 6 weeks, a finely-ground specimen had its original weight and m. p. and a sulphur content of 12·6%.

2 : 3-*Thionyldihydroxyanthracene* gives a bright golden-brown solution in cold concentrated sulphuric acid, and a pale yellowish-

green one in cold aqueous caustic soda. These solutions, when respectively diluted with water and acidified, deposit 2 : 3-dihydroxyanthracene. The thionyl compound is very sparingly soluble in hot alcohol, and the very pale yellow solution changes to dark greenish-yellow on addition of ferric chloride.

Action of acetic acid. When 1·1 g. of 2 : 3-thionyldihydroxyanthracene were added to 15 c.c. of boiling glacial acetic acid, very little dissolved and there was no detectable evolution of sulphur dioxide. The addition of two drops of pyridine, however, caused solution to occur with elimination of sulphur dioxide. After boiling for 2 hours, the solution was stirred into cold water; it then deposited 0·9 g. of a dull yellow precipitate, which was filtered off. In order to remove any mechanically-held acetic acid, the moist product was dissolved in hot alcohol, again precipitated with water, filtered off, and thoroughly washed. It was dried over sulphuric acid and examined quantitatively for the acetyl radical, which was absent. A hot acetic acid solution of the remainder of the product, on careful dilution with a warm aqueous solution of sulphur dioxide, deposited 2 : 3-dihydroxyanthracene in pale greenish-yellow plates; these melted at 280—282°, either alone or mixed with the pure compound (Found: C, 79·8; H, 4·9. Calc.: C, 80·0; H, 4·8%).

Action of acetic anhydride. A solution of 0·6 g. of 2 : 3-thionyldihydroxyanthracene in 8 c.c. of boiling acetic anhydride showed no signs of reaction until 1 drop of pyridine was added; sulphur dioxide was then detected. The solution was cooled after 1 hour, and diluted with alcohol; it deposited 0·3 g. of hexagonal plates of 2 : 3-diacetoxyanthracene, which, alone or mixed with an authentic specimen, melted at 175°. The filtrate, when stirred into water, yielded a further 0·4 g. of the same product (Found: $CH_3 \cdot CO$, 29·5. Calc.: $CH_3 \cdot CO$, 29·3%).

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed a portion of the expenses of this research, and also The British Alizarine Company, Limited, and I.G. Farbenindustrie Aktiengesellschaft, Leverkusen, for gifts of materials.

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[*Received, January 29th,* 1927.]

LXXXIV.—*Constitutional Studies in the Monocarboxylic Acids derived from Sugars. Part IV. The Isomeric Lactones obtained from Arabinose.*

By John Pryde and Robert William Humphreys.

With the view of accumulating more complete information regarding the isomeric forms of the pentose arabinose, we have continued our earlier investigations (Pryde, Hirst, and Humphreys, J., 1925, **127**, 348). Recently, Haworth and Nicholson (J., 1926, 1899) have had occasion to investigate related problems and in as far as our field and theirs have involved common ground we are able fully to corroborate their published findings.

We have now prepared 2 : 3 : 4-trimethyl arabonolactone from two different crystalline derivatives of arabinose, namely, the α- and β-stereoisomerides of trimethyl methylarabinoside. It has been shown by Hirst and Robertson (J., 1925, **127**, 358) that in the presence of acid methyl alcohol these two crystalline derivatives change in optical rotation until a final common equilibrium value of $[\alpha]_D + 150°$ is reached. Such evidence is generally accepted as showing that they are interconvertible α- and β-varieties of the same trimethyl methylarabinoside, possessing one and the same type of oxide linking. It has been clearly established that trimethyl α-methylarabinoside possesses an amylene-oxide linking (Hirst and Robertson, *loc. cit.*), but direct evidence regarding the β-compound is lacking. This evidence we are now able to supply in that it is shown that the crystalline β-compound yields on oxidation a lactone identical in optical rotation and in other physical properties with that obtained from the α-compound. The two stereoisomerides of the parent methylated sugar must therefore possess one and the same type of oxide linking. This is, so far as we are aware, the first *direct* chemical proof that two crystalline stereoisomeric sugars do in fact have a common oxide-linking structure.

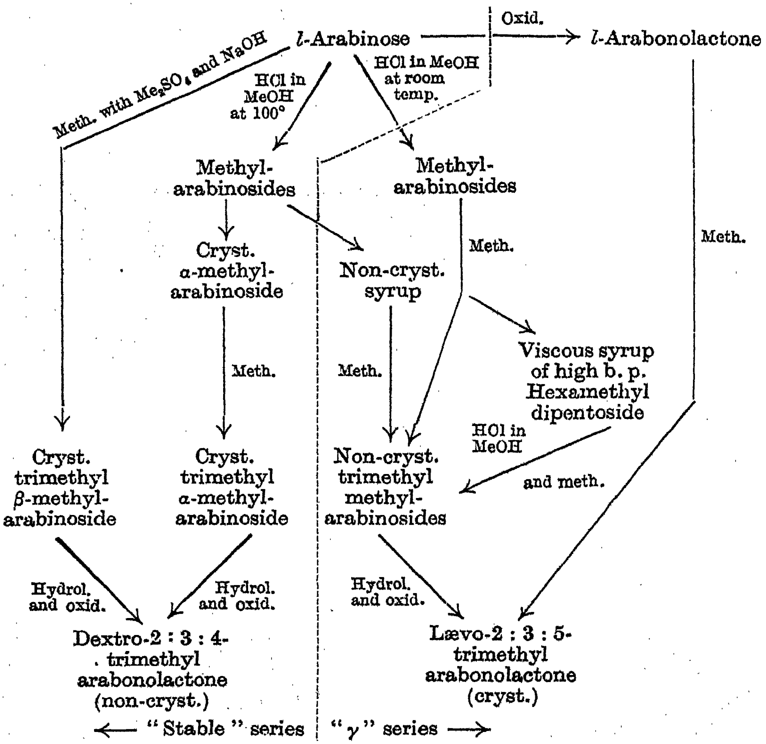
The isomeric 2 : 3 : 5-trimethyl arabonolactone has also been prepared from two different sources, namely, by synthesis of the mixed methyl γ-arabinosides and subsequent methylation, followed by simultaneous hydrolysis and oxidation with hydrobromic acid and bromine, and alternatively by bromine oxidation of arabinose followed by methylation. The crystalline lactones obtained by both these processes again proved to be identical with each other, but sharply distinguished in their physical and chemical properties from the liquid 2 : 3 : 4-trimethyl lactone. After the completion of this work, similar results obtained by slightly different methods were recorded by Haworth and Nicholson (*loc. cit.*). Particulars of our own preparations are summarised in the following table:

Starting material.	$[\alpha]_D$ in water.	M. p.	Product.	Initial $[\alpha]_D$ in water.	M. p.
Trimethyl α-methyl-*l*-arabinoside.	+250°	44—46°	2 : 3 : 4-Trimethyl arabonolactone.	+176·5°	Liq.
Trimethyl β-methyl-*l*-arabinoside.	+ 26·2	46	,, ,,	+178·3	Liq.
Trimethyl methyl-*l*-γ-arabinosides.	− 56*	Liq.	2 : 3 : 5-Trimethyl arabonolactone.	− 42·5	29°
l-Arabonolactone.	− 62	Syrup.	,, ,,	− 43·0	30

* Equilibrium rotation.

The combined results of these four methods of preparing the two isomeric lactones afford clear proof that the stereoisomeric α- and β-derivatives of the normal form of arabinose have a common oxygen linking of the 1 : 5 type, and that a change in the position of this linking to the 1 : 4 type completely alters the nature of the derivatives obtained.

In the course of the foregoing investigations, two further observations of considerable interest were made. Pryde, Hirst, and Humphreys (*loc. cit.*) have already shown that the anomalous rotations obtained in various preparations involving the preliminary condensation of arabinose with methyl alcohol at 100° are to be ascribed to the formation of mixtures of amylene- and butylene-oxidic forms. Evidence has now been obtained which affords a direct proof of this, and of which details will be found in the experimental section of this paper. Levene and Simms (*J. Biol. Chem.*, 1926, **68**, 737) have investigated a similar simultaneous formation of 1 : 5- and 1 : 4-lactone rings in the instance of gluconic acid. The second observation referred to above clearly demonstrated the tendency of γ-arabinose derivatives to enter into an auto-condensation forming a compound apparently of the dipentoside type. The conditions which led to this interesting condensation are being further investigated and publication of the experimental details is deferred until a later date. This brief reference is made here for the purpose of including the observation in the scheme which follows. Of some 11 g. of mixed methyl-γ-arabinosides, which had been prepared by the cold acid methyl alcohol method, it was found that some 6—7 g. had undergone auto-condensation to form a dipentoside, which was eventually reconverted into the simple methylated monopentoside in very good yield.


l-Arabinose
Oxid.
l-Arabonolactone
Meth. with Me₂SO₄ and NaOH
HCl in MeOH at 100°
HCl in MeOH at room temp.
Methyl-arabinosides
Methyl-arabinosides
Meth.
Cryst. α-methyl-arabinoside
Non-cryst. syrup
Meth.
Viscous syrup of high b. p. Hexamethyl dipentoside
Meth.
Meth.
HCl in MeOH
and meth.
Cryst. trimethyl β-methyl-arabinoside
Cryst. trimethyl α-methyl-arabinoside
Non-cryst. trimethyl methyl-arabinosides
Hydrol. and oxid.
Hydrol. and oxid.
Hydrol. and oxid.
Dextro-2 : 3 : 4-trimethyl arabonolactone (non-cryst.)
Lævo-2 : 3 : 5-trimethyl arabonolactone (cryst.)
← "Stable" series
"γ" series →

EXPERIMENTAL.

Preparation of 2 : 3 : 4-*Trimethyl Arabonolactone from Trimethyl* α-*Methylarabinoside*.—This preparation has been described by Pryde, Hirst, and Humphreys (*loc. cit.*). It only remains to add that later preparations of the lactone yielded products with higher initial specific rotations in water, but with identical equilibrium values. Thus, initial values of + 176°, falling to + 21·4° and 21·95° on equilibration in water, and 21·55° from the sodium salt have been obtained (compare the earlier values of + 145°, equilibrating to 22·4° in water, and 22·9° from the sodium salt).

Preparation of 2 : 3 : 4-*Trimethyl Arabonolactone from Trimethyl* β-*Methylarabinoside*.—The crystalline trimethyl β-methylarabinoside was obtained by direct methylation of *l*-arabinose by sodium hydroxide and methyl sulphate as described by Hirst and Robertson (*loc. cit.*). It had an initial $[\alpha]_D$ + 26·17° in methyl alcohol, an equilibrium value, after heating in acid methyl alcohol, of $[\alpha]_D$ + 151·6°, and m. p. 46°. It was converted into the lactone by treatment with hydrobromic acid and bromine by the method described by Pryde, Hirst, and Humphreys (*loc. cit.*). The lactone was obtained as a colourless, mobile syrup (Found: C, 50·4; H, 7·4; OMe, 47·9. Calc.: C, 50·5; H, 7·4; OMe, 48·9%), which had an initial $[\alpha]_D$ in water ($c = 1{\cdot}12$) $+ 178{\cdot}3°$, falling in 24 hours to an equilibrium value $[\alpha]_D + 21{\cdot}5°$. The equilibrium value determined from the sodium salt ($c = 0{\cdot}94$) was $+ 22{\cdot}13°$. 0·102 G. of lactone required 5·35 c.c. of $N/10$-alkali (calc., 5·40 c.c.).

Preparation of 2 : 3 : 5-*Trimethyl Arabonolactone from Trimethyl Methyl-γ-arabinosides.*—The trimethyl methyl-γ-arabinosides were obtained as a syrupy mixture by the method of Baker and Haworth (J., 1925, **127**, 365). During the formation of the methyl-γ-arabinosides a minimum specific rotation of $- 42{\cdot}8°$ was observed some 28 hours after the complete solution of the arabinose in the cold acid methyl alcohol, whilst in a second preparation a minimum value of $- 47{\cdot}14°$ was recorded. In the latter case, the syrupy product, when isolated, showed $[\alpha]_D - 47{\cdot}55°$ ($c = 1{\cdot}152$). Methylation with sodium hydroxide and methyl sulphate followed by Purdie's reagents yielded a syrup with the composition of trimethyl methylarabinoside, which, after distillation in a high vacuum, had $n_D^{15{\cdot}5°}$ 1·4370 and $[\alpha]_D$ in water $- 33{\cdot}62$ ($c = 0{\cdot}81$), in methyl alcohol $- 34{\cdot}37°$ ($c = 0{\cdot}91$), and an equilibrium rotation, after heating for 5 hours in acid methyl alcohol, of $[\alpha]_D - 56{\cdot}33°$. These results are all in good accord with those of Baker and Haworth. These authors isolated trimethyl-γ-arabinose by hydrolysis of the fully methylated arabinoside, and oxidised the free sugar to the corresponding monocarboxylic acid by means of nitric acid. In the present communication, simultaneous hydrolysis and oxidation of the arabinoside was achieved by using hydrobromic acid containing bromine. From 17 g. of trimethyl methyl-γ-arabinosides there were obtained, after vacuum distillation, 14 g. of a mobile liquid, b. p. 115°/2 mm., $n_D^{17°}$ 1·4452. This product soon solidified, yielding crystals which had m. p. 29° after being dried on porous tile (Found: C, 50·4; H, 7·3; OMe, 48·5. Calc.: C, 50·5; H, 7·4; OMe, 48·9%). 0·1355 G. of lactone required 7·15 c.c. of $N/10$-alkali (calc., 7·11 c.c.). $[\alpha]_D$ in water $- 42{\cdot}53°$, after 10 days $- 34{\cdot}5°$ ($c = 1{\cdot}12$). It is obvious from these figures that the lactone is identical with that obtained by Baker and Haworth by a different method. The lactone did not reduce Fehling's solution even on boiling, but instantly reduced alkaline permanganate in the cold.

Preparation of 2 : 3 : 5-*Trimethyl Arabonolactone from* l-*Arabonolactone.*—A similar preparation has been described by Haworth and Nicholson (*loc. cit.*), but the present work was completed prior to the publication of their results. Their methods differ somewhat from our own, and the following brief description of the latter is given. 15 G. of *l*-arabinose in 80 c.c. of water were shaken with 30 g. of bromine for 3 hours until solution was complete. The solution was then heated on a water-bath at 40°, and after 20 hours all reducing action had disappeared. The excess of bromine and the hydrobromic acid were removed in the usual manner and finally there were obtained 14·3 g. of arabonic acid as a pale yellow, viscous syrup. Great difficulty was experienced in converting this completely into the lactone, for even after treatment over phosphorus pentoxide at 100°/1 mm. the value of the specific rotation was only − 62°, whereas Fischer and Piloty (*Ber.*, 1891, **24**, 4214) record − 73·9° for their crystalline lactone. We did not obtain the lactone in a crystalline condition, owing either to its content of some 10% of unchanged arabonic acid, or more probably to the fact that it was not allowed sufficient time to crystallise. It was decided to subject the non-crystalline product to methylation.

Methylation of l-*Arabonolactone.*—This was carried out by means of Purdie's reagents, methyl alcohol being used as extraneous solvent in the first two methylations. During the removal of solvent in the recovery of the methylated product after the first methylation, a little methyl oxalate distilled over, showing the presence of a small amount of oxalic acid in our original preparation of the lactone. After a third methylation in the absence of an extraneous solvent, some 12 g. of a pale yellow, mobile syrup were obtained which on distillation gave the following fractions:

Fractions	I	II	III
Weight (g.)	0·5	10	0·5
B. p. at 1 mm.	70°	95—105°	130—140°
$n_D^{14°}$	1·4150	1·4450	1·4462
OMe %	57·4	53·1	45·2

(Calc. for methyl tetramethylarabonate, methyl trimethylarabonate, and trimethyl arabonolactone: OMe, 65·7, 55·8, and 48·9%, respectively.)

Fraction I obviously contained some methyl tetramethylarabonate and hence fractions II and III only were submitted to a fourth methylation and again distilled. The main portion (8 g.) distilled at 100—105°/1 mm. It had $n_D^{15°}$ 1·4396, OMe 55·0%, and $[\alpha]_D$ in water − 8·4° ($c = 1·21$). This product is therefore essentially the methyl ester of trimethylarabonic acid.

Hydrolysis of the Ester and Preparation of 2 : 3 : 5-*Trimethyl Arabonolactone.*—7 G. of the ester were hydrolysed with approximately *N*-barium hydroxide at 85°. The barium was quantitatively precipitated as the sulphate and, the filtrate being worked up in the usual way, 5 g. of a colourless, mobile liquid were collected at 106°/1 mm. This had $n_D^{15°}$ 1·4452 and soon formed a solid mass of white crystals, m. p. 30°, after drying (Found : C, 50·3; H, 7·4; OMe, 48·3. Calc.: C, 50·5; H, 7·4; OMe, 48·9%). 0·0989 G. of lactone required 5·26 c.c. of N-alkali (calc., 5·20 c.c.). It showed an initial $[\alpha]_D$ − 43·05° in water ($c = 1·0$), changing after 7 days to − 35·5° and after 20 days to − 25·46°. This aqueous solution still behaved essentially as a lactone on titration, showing that only partial conversion into the acid had occurred. The following alterations of specific rotation were observed on acidifying a solution of the sodium salt ($c = 1·01$); the times recorded are from the moment of adding excess of acid: 2 mins. − 4·1°; 3 mins. − 5·03°; 6 mins. − 7·58°; 60 mins. − 24·29°; 24 hours − 26·23° ($t = 18°$). The free acid must therefore have a specific rotation of the order − 2°. The same equilibrium mixture of acid and lactone is obtained whether one starts with the lactone or with an acidified solution of the sodium salt.

Direct Proof of the Simultaneous Formation of Amylene- and Butylene-oxidic Forms of Arabinose Derivatives.—From a mixture of methylarabinosides obtained by the initial condensation of *l*-arabinose in acid methyl alcohol at 100°, the α-methylarabinoside was separated in a crystalline form, and this on subsequent methylation and oxidation was found to yield *d*-2 : 3 : 4-trimethyl arabonolactone. The residual mother-liquor from the crystalline α-methylarabinoside was evaporated to a syrup, and the product (10 g.) was methylated twice with sodium hydroxide and methyl sulphate and once by Purdie's reagents. The methylated product was then distilled in a high vacuum, and the main fraction (about 6 g.) distilled at 94°/0·5 mm. It had OMe, 59·0% (calc., 60·2%). As the original syrup separated from the crystalline α-arabinoside was naturally thought to be in large part the corresponding β-derivative, the distilled, fully methylated product was expected to yield crystalline 2 : 3 : 4-trimethyl β-methylarabinoside. No crystallisation could, however, be induced even on nucleating with a crystal of trimethyl β-methylarabinoside. Nucleation with a crystal of the α-stereoisomeride likewise gave a negative result. The product had a specific rotation in water of − 15°, and this lævorotation was assumed to indicate the presence of the γ-, *i.e.*, the butylene-oxidic, form of the sugar. This was fully confirmed on subjecting the liquid to simultaneous hydrolysis and oxidation in the usual manner. There was obtained a final product which, on being cooled and nucleated with a crystal of 2 : 3 : 5-trimethyl arabonolactone, yielded about 4 g. of crystals. These were purified on a tile and were found to be identical in every way with 2 : 3 : 5-trimethyl arabonolactone, having m. p. 29° and $[\alpha]_D$ − 42·4° ($c = 1·02$). It is thus clear that the original condensation of arabinose with methyl alcohol in the presence of hydrogen chloride at 100° must have resulted in the simultaneous formation of derivatives of the amylene- and butylene-oxidic types. It would also appear that only a relatively small amount of the β-stereoisomeride of the stable (amylene-oxidic) derivative was formed, since none could be separated from the fully methylated arabinoside product, and the final yield of butylene-oxidic lactone, allowing for experimental losses, was not far short of what might be expected had the whole of the non-crystalline syrup consisted of the butylene-oxidic form.

The expenses of this research were defrayed in part by a grant from the Medical Research Council, to whom we wish to express our grateful thanks. We are also indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (R. W. H.).

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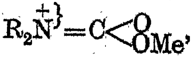
CARDIFF. [*Received, November 24th*, 1926.]

LXXXV.—*Nature of the Alternating Effect in Carbon Chains. Part XII. Nitration of some Derivatives of Methyl Benzylaminoformate.*

By JOHN WILLIAM BAKER.

IT has recently been shown (Goss, Ingold, and Wilson, J., 1926, 2440) that the acetyl derivatives of benzylamine, methylbenzylamine, and dibenzylamine nitrate mainly in the *op*-positions, it being assumed that the dissociation of the entity $R_3\overset{+}{N}\!:\overset{x}{\underset{x}{\vdots}}\,\overset{-}{H}\!:\overset{y}{\underset{y}{\vdots}}\,O{\cdot}NO_2$ (I) at *xx* becomes important and leads to the formation of a smaller amount of the *m*-isomeride than in the cases of the corresponding unacetylated bases. It was also assumed that the nitrogen atom does not acquire a sufficiently strong or permanent charge by betaine isomerisation for any considerable *m*-substitution to arise from this cause.

In order, if possible, to obtain further information as to the relative effects of these two opposing influences (internal and external ammonium-salt formation), it was considered of interest to determine the behaviour on nitration of the corresponding methyl benzylaminoformates, $C_6H_5{\cdot}CH_2{\cdot}NR{\cdot}CO_2Me$ (II), which are constituted similarly to the acetobenzylamides in so far as concerns the possibility of betaine isomerisation,  $R_2\overset{+}{N}\}{=}C{<}\begin{smallmatrix}O\\OMe\end{smallmatrix}$, excepting that, presumably owing to this cause, their basicity appears to be less. The present communication deals with the nitration of methyl benzyl-, dibenzyl-, and benzylmethyl-aminoformates (II; R=H, CH_2Ph, and Me, respectively). These substances are less basic than the corresponding acetyl derivatives; *e.g.*, acetomethylbenzylamide is completely soluble in cold 3% hydrochloric acid, whilst the benzylmethylaminoformate is soluble only in concentrated acid; acetodibenzylamide is easily soluble in concentrated hydrochloric acid, whereas the dibenzylaminoformate is almost insoluble. Hence it would be expected that dissociation of the salt (I) at *yy* (promoting meta-substitution) will be somewhat less, and at *xx* (promoting primarily *op*-substitution) somewhat greater, in the urethanes than in the corresponding acetobenzylamides. On the other hand, the urethanes would probably have a greater tendency towards a betaine phase, so that it is difficult to foretell how the proportions of meta-isomeride formed on nitration should compare with those obtained from the acetyl compounds; they should, however, be of the same order of magnitude, and therefore considerably less than those obtained from the corresponding unsubstituted bases.

Whilst great accuracy cannot be claimed for the figures obtained where only small quantities of the *m*-compound are produced (compare the following paragraph), the actual proportions of meta-isomeride found in the cases considered, $C_6H_5{\cdot}CH_2{\cdot}NR{\cdot}CO_2Me$, are as follows: R = Bz, 14%; R = Me, 12%; R = H, 11%; the corresponding figures for the acetyl derivatives, $C_6H_5{\cdot}CH_2{\cdot}NRAc$, being R = Bz, 25%; R = Me, 8%; R = H, 7%; whilst those of the unsubstituted bases, $C_6H_5{\cdot}CH_2{\cdot}NHR$, are, respectively, 76%, 69%, and 44%.

Unfortunately, the determination of the meta-content of the nitration mixtures by the bromate-titration method (Goss, Ingold, and Wilson, *loc. cit.*) was possible only in the case of the dibenzyl compound (see p. 571), and, moreover, the experimental error in this method is relatively great when only small amounts of the meta-isomeride are present. A method, based on that given by Holleman (*Rec. trav. chim.*, 1899, **18**, 268) and believed to be, when applicable, a definite improvement on the preceding one, was tested in this investigation with a view to its use in future cases in which only very small amounts of meta-isomeride might have to be estimated. In principle, the method depends on the extraction, at a constant temperature, of a known weight of the mixed nitrobenzoic acids, formed on oxidation of the nitration product, with a solution saturated with respect to the *o*- and *p*-isomerides and determination of the increase in acidity due to the dissolved meta-compound by titration with standard (*N*/100) baryta solution. Subsequent extraction with a solution saturated with respect to the *o*-, *p*-, and *m*-acids allows a correction to be applied for any small amount of foreign acid matter present. Full details will be found in the experimental portion of this paper, and the results show that the method gives moderately consistent values for the meta-content of the mixtures.

EXPERIMENTAL.

A. *Preparation of Derivatives of Methyl Benzylaminoformate.*

Methyl benzylaminoformate was prepared by the method of Wieman and Jongkees (*Rec. trav. chim.*, 1906, **25**, 243) and had m. p. 62—64° (Found : N, 8·5. Calc. : N, 8·5%).

Methyl Benzylmethylaminoformate.—A solution of methyl chloroformate (2·7 g.) in dry ether was added dropwise with efficient cooling to an ethereal solution of benzylmethylamine (Holmes and Ingold, J., 1925, **127**, 1813) (3·5 g.). A vigorous action took place and the hydrochloride of the base separated. This was decomposed by a slight excess of 10% caustic soda solution, a second molecule (2·7 g.) of methyl chloroformate added, and after a while the whole was acidified with hydrochloric acid and shaken with ether. The residue obtained from the ethereal solution (dried with sodium sulphate) was a colourless, viscous liquid, which was distilled twice under reduced pressure. *Methyl benzylmethylaminoformate* has b. p. 118°/5 mm. (Found : C, 66·3, 66·8; H, 7·5, 7·2; N, 7·5. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8%).

Great difficulty was experienced in proving the purity of this compound, due, it was subsequently found, to the production of methane during combustion. In order to ensure its purity, benzylmethylamine was fractionated twice under reduced pressure and converted into its hydrochloride by the action of dry hydrogen chloride in dry ether, the hydrochloride was crystallised from absolute alcohol, and the regenerated base again distilled under reduced pressure. This purified specimen and freshly-distilled methyl chloroformate in equimolecular proportion were mixed, with cooling, in dry ethereal solution, the hydrochloride of the base that separated was filtered off, and the methyl benzylmethylaminoformate obtained from the ethereal solution was twice carefully distilled under reduced pressure. The specimen so obtained was a colourless, highly refractive liquid, b. p. 118°/5 mm. On analysis under ordinary conditions, it gave C, 64·6; H, 7·3%, but when mixed with cuprous chloride and slowly burnt in a very hot combustion tube it gave the values recorded above. The gas obtained in the nitrogen determination (Dumas) contained 43·1% of combustible gas, of which 39·7% was methane, whence the value for the nitrogen content given above was calculated.

Methyl dibenzylaminoformate, obtained in a similar manner from methyl chloroformate and dibenzylamine, had b. p. 199°/13 mm. (Found : C, 75·0; H, 6·7. $C_{16}H_{17}O_2N$ requires C, 75·4; H, 6·7%).

Methyl pp′-*dinitrodibenzylaminoformate* was prepared by the condensation of *pp*′-dinitrodibenzylamine with methyl chloroformate. After crystallisation from ethyl acetate–ligroin it had m. p. 140° (Found : C, 55·8; H, 4·5. $C_{16}H_{15}O_6N_3$ requires C, 55·6; H, 4·4%).

Methyl p-*nitrobenzylaminoformate* was obtained by adding 2·4 g. of methyl chloroformate to molten *p*-nitrobenzylamine (45°), the reaction mixture being diluted with dry ether when it became too solid owing to the separation of the hydrochloride of the base. Isolated as above and crystallised from absolute alcohol, the product had m. p. 109·5° (Found: C, 51·4; H, 4·9. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%).

B. *Nitration of the Benzylaminoformates and Determination of the Proportion of* m-*Isomeride : General Procedure.*

The conditions of nitration were similar in all three cases studied, the aminoformate being run in (or added in small successive portions if a solid) at the rate of approximately 1 g. per hour to mechanically stirred nitric acid (*d* 1·442 : acid of greater density produces a large proportion of dinitrated compounds) at 0°. The isolation of the product varied somewhat from case to case and is described below.

As stated in the introduction, the bromate-titration method gave trustworthy results only for methyl dibenzylaminoformate. In the other cases, the proportion of *m*-isomeride was determined by the solubility method described below.

In each of four 200 c.c. stoppered bottles (*A*, *B*, *C*, and *D*) were placed 80 c.c. of a solution of *o*- and *p*-nitrobenzoic acids saturated at 24°, together with some of the pure solid acids in order to ensure saturation. *A* served as a control. Into *B*, *C*, and *D* were weighed quantities (about 1 g.) of the mixtures of nitrobenzoic acids obtained by oxidation of the nitration products, the weight in each being such that the quantity of *m*-acid was considerably less than that required to saturate the 80 c.c. of water present. The four bottles were fixed in a frame and rotated for 36—48 hours in an electrically controlled thermostat at 24·5° (±0·5°). They were kept stationary at the same temperature for a further period of 24 hours and the clear supernatant liquors were then filtered, the first few c.c. being rejected, since a certain error is otherwise introduced owing to slight adsorption on the filter-paper. All the operations, except the final titration, were carried out in the thermostat, and all the apparatus used was stored therein. An aliquot portion (10 c.c.) of each filtrate was withdrawn (in pipettes calibrated relatively to one another) and titrated with $N/100$-baryta and phenolphthalein. The residual untitrated liquors were returned to their respective flasks and to each was added sufficient pure *m*-nitrobenzoic acid to saturate it, and the operations were repeated. The differences between the volumes of baryta required for *B*, *C*, and *D*, respectively, and the volume required for *A* represent the amounts of foreign acid present which must be subtracted from the volume differences found in the first titrations in order to give correct values for the *m*-nitrobenzoic acid present. Holleman (*loc. cit.*) found that the solubility of the *o*- and *p*-acids increased in the presence of an appreciable quantity of the *m*-isomeride, and therefore a correction curve was plotted from the following figures, obtained in preliminary determinations of small, weighed amounts of *m*-isomeride added:

Meta added	14·6	19·5	23·3	39·4	54·0	61·2	87·2	115·1 mg.
Meta found	13·0	15·0	22·2	38·6	52·7	66·6	92·9	133·4 ,,

C. *Details of Individual Cases.*

I. *Methyl Dibenzylaminoformate.—Experiment* 11. The nitration product was poured on crushed ice and made alkaline by the addition of potassium hydroxide solution. The somewhat sticky precipitate produced was filtered off and washed free from gum with a large volume of ether (it dissolved and almost immediately crystallised). The aqueous filtrate was extracted with ether, and the combined extract and washings were worked up in the usual manner, yielding a very viscous gum which slowly solidified (total yield, 94% of the theoretical) [Found for the crystalline solid (30% of the product): C, 55·9; H, 4·6. Found for the gum (70%): C, 55·1; H, 4·4. $C_{16}H_{15}O_6N_3$ requires C, 55·6; H, 4·4%]. The titration of the pure *p*-nitro-isomeride gave a mean bromination number (compare Goss, Ingold, and Wilson, *loc. cit.*) $F = 2·175$, whilst for the crystalline solid and the gum were found $F = 2·373$ and 2·282, respectively, representing meta-contents of 20% and 11%, respectively. Hence the meta-content of the whole nitration product is (20% of 30%) + (11% of 70%) = 14%.

Experiment 12. The nitration product obtained from 5·0 g. of methyl dibenzylaminoformate was separated into three fractions: (α) a solid, 1·44 g., m. p. 132—135°; (β) a second solid fraction, 2·482 g., m. p. 100—103°, which crystallised from the ethereal extract; and (γ) a residual gum, 2·374 g. (total yield, 93% of the theoretical) [Found: (α) C, 55·9; H, 4·6; (β) C, 55·9; H, 4·7; (γ) C, 55·8; H, 4·6%]. Each fraction was separately titrated by the bromate method and gave bromination numbers α, 2·195; β, 2·225; γ, 2·435, corresponding to respective meta-contents of 2%, 5%, and 26%, whence the meta-content of the whole nitration product is 13%. Fraction (γ) was oxidised by potassium permanganate to the mixed nitrobenzoic acids (yield, 64%) (Found: *M*, by titration, 165·8. Calc.: *M*, 167), which were separated by the method of Baker and Ingold (J., 1926, 2469). The separated *p*-acid (57%) had m. p. 210—215°; after crystallisation from water it had m. p. 232° (mixed m. p. with pure *p*-acid, 237°). The separated *m*-acid (19%) had m. p. 122°, which was raised to 136° by crystallisation from ethyl acetate–ligroin (mixed with the pure *m*-acid, it melted at 141°). Crystallisation of the fraction α from ethyl acetate–ligroin gave pure methyl *pp*′-dinitrodibenzylaminoformate, which, alone or mixed with a synthetic specimen, melted at 140°.

II. *Methyl Benzylmethylaminoformate.—Experiment* 21. The nitration product was poured on crushed ice, an oil being precipitated, and was made alkaline with potassium hydroxide solution; the whole was then extracted with ether. The gum obtained from the dried ethereal extract failed to crystallise (yield, 92·5% of the theoretical) (Found: C, 54·4; H, 5·8. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4%). A further 3% of the material was accounted for as an acid fraction produced by oxidation during the nitration. The neutral nitration product was oxidised with boiling 2% potassium permanganate solution (yield, 77%), and the content of *m*-acid in the mixed nitrobenzoic acids produced (Found: *M*, by titration, 162. Calc.: *M*, 167) was determined by the solubility method: 0·6052 g. required 48·00 c.c. of 0·01029*N*-baryta for the *m*-acid present; this corresponds to 0·08251 g. of *m*-acid, which becomes 0·0735 g. after correction. The content of *m*-acid is therefore 12%.

III. *Methyl Benzylaminoformate.—Experiment* 33. The nitration product, worked up as in the previous case, gave a solid (yield, 81%) (Found: C, 51·1; H, 4·8. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%) which, after crystallisation from ethyl alcohol, had m. p. 109·5°. This consisted of the pure *p*-nitro-compound, since it gave no m. p. depression in admixture with a synthetic specimen and on oxidation with 2% potassium permanganate solution gave pure *p*-nitrobenzoic acid, m. p. 237° (alone or mixed with a genuine specimen). Determinations of the content of *m*-acid by the bromate method gave bromination numbers of $F = 2·850$, 2·880, 2·850, 2·900. The values of *F* for the pure *p*- and *m*-isomerides are, however, 2·870 and 3·050, respectively. The difference is too small for this method to give trustworthy results.

Experiment 34. The nitration product (yield, 83%, a further 6% being accounted for as acid products) (Found: C, 51·2; H, 5·0%) was oxidised with 2% potassium permanganate solution (yield, 86%), and the meta-content of the resulting mixture of nitrobenzoic acids (Found: *M*, by titration, 165·6. Calc.: *M*, 167) determined by the solubility method: 0·8424 g. of the mixed acids required 59·84 c.c. of 0·01029*N*-baryta for the *m*-acid present; this corresponds to 0·1029 g. of *m*-acid, which becomes 0·091 g. after correction. The content of *m*-acid is therefore 11%.

The author wishes to express his gratitude to Professor C. K. Ingold, F.R.S., for his kindly interest and advice during the course of this investigation, and to the Government Grant Committee of the Royal Society for a grant towards the expense.

THE UNIVERSITY, LEEDS. [*Received, November 29th,* 1926.]

LXXXVI.—*Elimination of the Amino-group of Tertiary Amino-alcohols. Part IV. The Displacement of the Amino- by the Hydroxy-group.*

By ALEX. MCKENZIE and ROBERT ROGER.

As was stated in Part I (J., 1923, **123**, 79) of this series of papers, the study of the deamination of tertiary amino-alcohols was initiated from its bearing on the rôle of nitrous acid in the Walden inversion. It was anticipated that the action of nitrous acid on an optically active amino-alcohol, such as *d*-β-hydroxy-αββ-triphenylethylamine, would proceed on the orthodox lines, and by giving either *d*- or *l*-triphenylethylene glycol would provide additional data for the Walden inversion:

$$d\text{-}C_6H_5\cdot CH(NH_2)\cdot CPh_2\cdot OH \longrightarrow d\text{- or } l\text{-}C_6H_5\cdot CH(OH)\cdot CPh_2\cdot OH.$$

It is, however, impossible to realise this change experimentally, as the product is invariably the optically inactive ketone, phenyldeoxybenzoin (J., 1925, **127**, 283). That this reaction, which involves the migration of a hydrocarbon residue, is a very general one is obvious from the following examples:

$$OH\cdot CPhR\cdot CHR'\cdot NH_2 \longrightarrow R\cdot CO\cdot CHPhR'$$

(R = R′ = Ph: J., 1923, **123**, 79; 1925, **127**, 283.
R = Me; R′ = Ph: J., 1923, **123**, 79; 1924, **125**, 844.

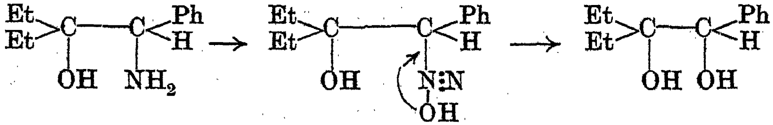
$R = C_{10}H_7$; $R' = Ph$: J., 1924, **125**, 2105; Orékhov and Tiffeneau, *Compt. rend.*, 1924, **178**, 1619.
*$R = Ph$; $R' = Me$: J., 1925, **127**, 283.
*$R = Ph$; $R' = CH_2Ph$: J., 1925, **127**, 283.
$R = Ph$; $R' = H$: Bettzieche, *Z. physiol. Chem.*, 1924, **140**, 273; Orékhov and Roger, *Compt. rend.*, 1925, **180**, 70.)

$$OH{\cdot}CRR'{\cdot}CHR''{\cdot}NH_2 \longrightarrow R{\cdot}CO{\cdot}CHR'R''$$

($R = Ph$; $R' = C_6H_4{\cdot}OMe$; $R'' = H$: Orékhov and Roger, *loc. cit.*
$R = Ph$; $R' = C_{10}H_7$; $R'' = H$: Luce, *Compt. rend.*, 1925, **180**, 145.
$R = R' = CH_2Ph$; $R'' = Ph$: J., 1926, 779; Bettzieche and Ehrlich, *Z. physiol. Chem.*, 1925, **150**, 197.)

Despite the regularity with which a hydrocarbon residue migrates in those reactions, we thought that it might be possible to select a suitable amino-alcohol in which the normal displacement of the amino- by the hydroxy-group could be effected by the aid of nitrous acid. This has now been accomplished in two instances, in one of which the glycol was the main product, whilst in the other the glycol also was isolated, although the main product was the ketone.

When β-amino-αα-diethyl-β-phenylethyl alcohol, prepared by the method of Thomas and Bettzieche (*Z. physiol. Chem.*, 1924, **140**, 244), was acted on by nitrous acid, the crystals which were isolated consisted of α-phenyl-ββ-diethylethylene glycol, which had previously been prepared by Tiffeneau and Lévy from magnesium ethyl bromide and ethyl *dl*-mandelate (*Bull. Soc. chim.*, 1923, **33**, 735). The mechanism of the action may be outlined as follows :



As in semipinacolinic deamination, the formation of an intermediate unstable diazo-compound is assumed, but water is not produced, the hydroxy-group migrating from nitrogen to carbon. No transposition of the ethyl group was detected.

The main product of the deamination of β-amino-β-phenyl-αα-dibenzylethyl alcohol, prepared by the action of magnesium benzyl chloride on ethyl *r*-phenylaminoacetate hydrochloride, is benzyl αβ-diphenylethyl ketone (J., 1926, 779), but the mother-liquors from which this ketone had been crystallised gradually deposited crystals from which α-phenyl-ββ-dibenzylethylene glycol, m. p. 115—116°, has now been isolated. The identity of this glycol was established by comparison with the compound prepared from magnesium benzyl chloride and ethyl *dl*-mandelate (Orékhov, *Bull. Soc. chim.*, 1919, **25**, 111). Here, semipinacolinic deamination was accompanied by the ultimate displacement of the amino- by the hydroxy-group :

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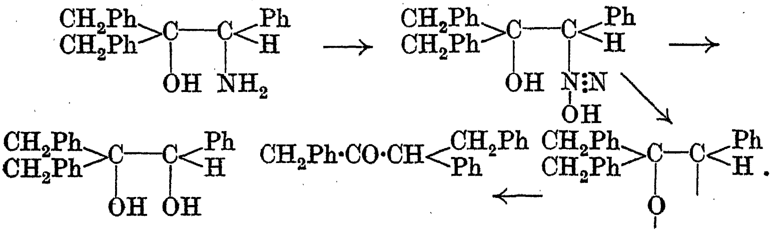
* The preparation of optically active ketones from *d*-alanine, *d*-phenylalanine and *l*-phenylalanine has also been described (J., 1926, 779).

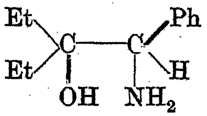


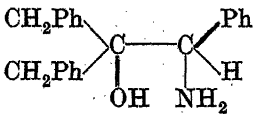
$$\begin{matrix}\mathrm{CH_2Ph}\\ \mathrm{CH_2Ph}\end{matrix}\!>\!\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\text{—}\underset{\mathrm{NH_2}}{\underset{|}{\mathrm{C}}}\!<\!\begin{matrix}\mathrm{Ph}\\ \mathrm{H}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CH_2Ph}\\ \mathrm{CH_2Ph}\end{matrix}\!>\!\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\text{—}\underset{\underset{\mathrm{OH}}{|}}{\underset{\mathrm{N{:}N}}{\underset{|}{\mathrm{C}}}}\!<\!\begin{matrix}\mathrm{Ph}\\ \mathrm{H}\end{matrix} \longrightarrow$$

$$\begin{matrix}\mathrm{CH_2Ph}\\ \mathrm{CH_2Ph}\end{matrix}\!>\!\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\text{—}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\!<\!\begin{matrix}\mathrm{Ph}\\ \mathrm{H}\end{matrix} \quad \mathrm{CH_2Ph{\cdot}CO{\cdot}CH}\!<\!\begin{matrix}\mathrm{CH_2Ph}\\ \mathrm{Ph}\end{matrix} \longleftarrow \begin{matrix}\mathrm{CH_2Ph}\\ \mathrm{CH_2Ph}\end{matrix}\!>\!\underset{\underset{|}{\mathrm{O}}}{\underset{|}{\mathrm{C}}}\text{—}\underset{|}{\mathrm{C}}\!<\!\begin{matrix}\mathrm{Ph}\\ \mathrm{H}\end{matrix}.$$

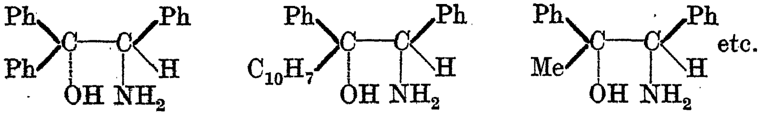
From several viewpoints, this normal action of nitrous acid which led to the formation of the two glycols presents points of interest. Thus, it renders the possibility open for the conversion, for example, of *l*-phenylaminoacetic acid into the configuratively-related diethyl-amino-alcohol, and the transformation of the latter into a glycol which could then be contrasted with that obtainable by the action of magnesium ethyl bromide on ethyl *l*-mandelate.

It will also be observed in those cases where nitrous acid behaved normally that the two hydrocarbon residues attached in the amino-alcohol to the carbon atom to which the hydroxy-group is also bound are groups with a small saturation capacity. Ample evidence of the low saturation capacity of both the ethyl and the benzyl group is provided by the important researches of Tiffeneau, Orékhov, and Mlle. Lévy. In the two amino-alcohols under discussion, the hydroxy-group is in each case firmly linked to the carbon atom, and semipinacolinic deamination would accordingly be retarded, if not entirely prevented. On this conception, the amino-alcohols could be depicted as follows :



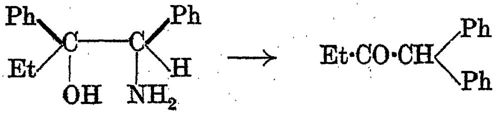


On the other hand, the striking fact emerges that in every instance of semipinacolinic deamination studied by us (with the exception of that of β-amino-β-phenyl-αα-dibenzylethyl alcohol), the strong saturation capacities of the hydrocarbon residues have caused the tertiary hydroxy-group to be comparatively loosely bound, thus:



When such compounds are acted on by nitrous acid, the hydroxy-group should readily combine with hydrogen with the elimination of water, and it actually does this.

It will also be noticed that in the examples quoted both of the hydrocarbon residues associated with the tertiary hydroxy-group have either weak or strong saturation capacities. An example is now described where one of the residues has a strong and the other a weak saturation capacity. A compound possessing this type of grouping was prepared by the action of magnesium ethyl iodide on desylamine hydrochloride, and it was found to undergo semipinacolinic change with nitrous acid:



The phenyl group migrated, the sole product isolated being diphenylbutanone. Now, the corresponding glycol, ethylhydrobenzoin, has been dehydrated by Tiffeneau and Orékhov (*Bull. Soc. chim.*, 1921, **29**, 422), who found that, under the influence of concentrated sulphuric acid, this glycol was transformed into a mixture of diphenylbutanone and ethyldeoxybenzoin. Our present experiments show that phenyl has a greater migrational aptitude than ethyl. Further, there was no evidence of the formation of ethylhydrobenzoin, and the hydroxy-group of the amino-alcohol was, therefore, less firmly bound than in the diethyl- or dibenzyl-amino-alcohols.

It should be emphasised that in addition to the effect of the ethyl and benzyl groups in causing the tertiary hydroxy-group to be firmly bound in β-amino-αα-diethyl-β-phenylethyl alcohol and in β-amino-β-phenyl-αα-dibenzylethyl alcohol, the phenyl group, which is attached to the same carbon atom as is the amino-group, would probably also be a contributory factor, although to a less degree than the ethyl and benzyl groups. The peculiar influence of the phenyl group has already been referred to by Mlle. Lévy in other connexions (*Bull. Soc. chim.*, 1923, **33**, 1655; 1926, **39**, 67).

It is also noteworthy that the best yield of glycol was obtained from that amino-alcohol in which the hydrocarbon residues attached to the tertiary carbon atom were purely aliphatic.

EXPERIMENTAL.

Deamination of β-Amino-αα-diethyl-β-phenylethyl Alcohol.—*r*-Phenylaminoacetic acid was converted into the hydrochloride (1 mol.) of its ethyl ester, which was then acted on by magnesium ethyl bromide (10 mols.). The resulting amino-alcohol (2 g.) was dissolved in 50% acetic acid, and an aqueous solution of sodium nitrite (2·2 g.) was gradually added, the temperature being maintained at 0°. Over-night, the oil had partly solidified; the product was extracted with ether, the extract washed with sodium bicarbonate, and the ether dried and expelled. The solid (1·6 g.) was crystallised thrice from light petroleum (b. p. 60—80°), from which it separated in needles containing no nitrogen, and melting at 89—89·5° (Found: C, 74·0; H, 9·4. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·3%). The product gave an orange coloration with concentrated sulphuric acid, and was α-phenyl-ββ-diethylethylene glycol, which has m. p. 89° according to Tiffeneau and Lévy (*loc. cit.*).

The mother-liquors yielded a small quantity of oil which may have contained some ketone from semipinacolinic deamination, although no semicarbazone was actually obtained from it.

To eliminate the possibility of the acetic acid having caused the elimination of the amino-group by hydrolysis, a control experiment on the above lines was carried out in which the addition of the sodium nitrite was omitted. No glycol was isolated.

Deamination of β-Amino-β-phenyl-αα-dibenzylethyl Alcohol.—The amino-alcohol was prepared by the action of magnesium benzyl chloride on ethyl phenylaminoacetate hydrochloride. An aqueous solution of sodium nitrite (2·3 g.) was gradually added to the solution of the amino-alcohol (3 g.) in glacial acetic acid (30 g.), the solution being kept at 0° and stirred vigorously. The viscous product did not solidify entirely when kept over-night, and, after the addition of water, it was extracted with ether, the ether extract washed with sodium carbonate, and dried with sodium sulphate. The resulting oil was dissolved by heating with light petroleum (b. p. 60—80°). After the crystals (A) which gradually separated had been removed, the filtrate was evaporated to dryness, and the oil dissolved in ethyl alcohol; crystals (B) which separated were united with (A) and crystallised from ethyl alcohol; 0·6 g. of benzyl αβ-diphenylethyl ketone (m. p. 74—74·5°) was then obtained. The ethyl-alcoholic solution from which (B) had been withdrawn gradually deposited a higher-melting solid, which after crystallisation from rectified spirit gave α-phenyl-ββ-dibenzylethylene glycol, m. p.

115—116°. Yield, 0·5 g. For comparison, the glycol was prepared by the action of magnesium benzyl chloride on ethyl *dl*-mandelate, and there was no depression of the melting point when samples from both sources were mixed.

In another experiment, conducted under somewhat similar conditions with dilute acetic acid (15%, 180 c.c.), 5 g. of the amino-alcohol were acted on by a solution of 4 g. of sodium nitrite. The yield of pure glycol was in this case 1·1 g.

Deamination of β-*Amino*-α-*ethyl*-αβ-*diphenylethyl Alcohol.*—Ten g. of desylamine hydrochloride (1 mol.), prepared by the reduction of benzil β-monoxime with stannous chloride according to Pschorr and Brüggemann (*Ber.*, 1902, **35**, 2740), were added in instalments within 2 hours to the Grignard reagent prepared from 57 g. of ethyl iodide (9 mols.). The temperature was maintained at about 0° during the addition. Over-night, the mixture was boiled gently for 2½ hours, and then decomposed by ice and dilute hydrochloric acid. The acid layer was separated and made alkaline with ammonia; the free amino-alcohol then separated as an oil. The latter was triturated with ice-cold concentrated hydrochloric acid, and the solid hydrochloride (11 g.) was collected and crystallised from dilute hydrochloric acid–ethyl alcohol.

β-*Amino*-α-*ethyl*-αβ-*diphenylethyl alcohol hydrochloride*, $NH_2{\cdot}CHPh{\cdot}CEtPh{\cdot}OH,HCl$, crystallises in rosettes of feathery needles, m. p. 224—226° (Found: Cl, 12·6. $C_{16}H_{19}ON,HCl$ requires Cl, 12·8%). It gives a transient pink coloration with concentrated sulphuric acid.

A solution of sodium nitrite (2 g.) was gradually added to a solution of the hydrochloride (2·2 g.) in dilute hydrochloric acid, and the resulting oil was extracted with ether. Yield: 2 g. This was acted on by semicarbazide hydrochloride and sodium acetate; 1·3 g. of the solid semicarbazone were then obtained. After crystallisation from rectified spirit, rectangular needles of the semicarbazone of diphenylbutanone separated. These melted at 195—196°, and there was no depression of the melting point on admixture with the semicarbazone of diphenylbutanone prepared by the dehydration of ethylhydrobenzoin with concentrated sulphuric acid.

We are indebted to Miss A. W. Cochrane, Miss M. S. Lesslie, and Mr. A. K. Mills for assistance in the preparative work. We also thank the Carnegie Trust for the award of a Fellowship to one of us.

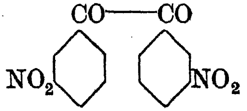
UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS.
[*Received, August 3rd,* 1926.]

LXXXVII.—*The Nitration of Benzil. 3:5:3′:5′-Tetranitrobenzil.*

By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY COULSON.

IT has recently been shown (Chattaway and Coulson, J., 1926, 1070) that when benzil is nitrated, a mixture of three isomeric dinitrobenzils is obtained, whether the nitration is effected by fuming nitric acid or by a mixture of potassium nitrate and sulphuric acid. The crude product, although consisting largely of 3 : 3′-dinitrobenzil (I), contains considerable amounts of the 2 : 3′- (II) and 2 : 2′-dinitrobenzil (III).

(I.)



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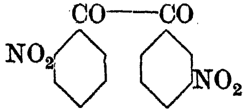

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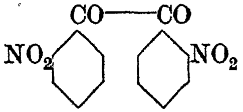
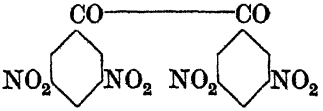


(IV.)



Barnett and Kay, who regarded this crude mixture as pure 3 : 3′-dinitrobenzil, were unable to nitrate it further (*Chem. News*, 1922, **125**, 57), whilst Christie and Kenner (J., 1926, 470) found no difficulty in doing this, and obtained a tetranitro-derivative (m. p. 168°) which must have been a mixture of isomerides.

3 : 3′-Dinitrobenzil having been isolated in a pure state, the further action of nitric acid upon it has been studied.

On nitration by a mixture of fuming nitric acid and sulphuric acid it yields 3 : 5 : 3′ : 5′-*tetranitrobenzil* (IV), m. p. 179°.

The only other substance produced in any recognisable quantity in the nitration is 3 : 5-dinitrobenzoic acid, which is formed in considerable amount as a by-product. That the entering nitro-groups take up the vacant *meta*-positions is shown by the production of an approximately theoretical amount of 3 : 5-dinitrobenzoic acid when the tetranitrobenzil is oxidised by chromic acid.

EXPERIMENTAL.

Isolation of 3 : 3′-Dinitrobenzil (I).—3 : 3′-Dinitrobenzil is most readily isolated from the product of the direct nitration of benzil (which melts at about 109°) by cooling rapidly a saturated acetone solution. A pulpy mass of crystals, melting not very sharply near 122°, separates, and a further crop of the 3 : 3′-isomeride, somewhat less pure, is obtained by distilling off part of the acetone from the mother-liquor. The process can be repeated several times until the 2 : 3′- and 2 : 2′-isomerides are seen among the crystals separating.

The various crops of crystals are then mixed and the process is repeated five or six times, until the melting point has been raised to about 129°. The final purification is best effected by recrystallising the material from acetic acid until the crystals melt sharply at 132°.

3 : 3′-*Dinitrobenzil monophenylhydrazone*,

$NO_2 \cdot C_6H_4 \cdot C(N \cdot NHPh) \cdot CO \cdot C_6H_4 \cdot NO_2$,

separates as a pulpy mass of yellow crystals when an alcoholic solution of 3 : 3′-dinitrobenzil (1 mol.) and phenylhydrazine (1 mol.) is boiled for about an hour. It crystallises from boiling acetic acid, in which it is easily soluble, in very slender, yellow prisms, m. p. 171° (Found : N, 14·7. $C_{20}H_{14}O_5N_4$ requires N, 14·4%).

3 : 3′-*Dinitrobenzil osazone*,

$NO_2 \cdot C_6H_4 \cdot C(N \cdot NHPh) \cdot C(N \cdot NHPh) \cdot C_6H_4 \cdot NO_2$,

although formed only in very small amount when an alcoholic or acetic acid solution of 3 : 3′-dinitrobenzil or its monophenylhydrazone is boiled with a great excess of phenylhydrazine, separates in considerable amount when phosphorus pentoxide is added to the reaction mixture.

1·5 G. of 3 : 3′-dinitrobenzil (1 mol.) was boiled with 1·5 g. of phenylhydrazine (3 mols.) and 2 g. of phosphorus pentoxide in acetic acid for an hour. On cooling, the osazone separated free from the monohydrazone. It crystallises from boiling acetic acid, in which it is only slightly soluble, in long, slender, bright yellow prisms, which, after drying on the water-bath, contain 1 mol. of acetic acid. This is lost when the compound is heated to 130—140°, the crystals becoming opaque and lighter in colour (Found : loss after heating at 140°, 10·9. $C_{26}H_{20}O_4N_6,CH_3 \cdot CO_2H$ requires loss, 11·1%). The osazone melts at 269° (Found : N, 17·2. $C_{26}H_{20}O_4N_6$ requires N, 17·5%).

2 : 3-*Di*(3′-*nitrophenyl*)*quinoxaline* separates when a solution of equivalent amounts of *o*-phenylenediamine and 3 : 3′-dinitrobenzil in acetic acid is heated. It dissolves sparingly in boiling acetic acid and separates in very pale yellow, rhombic plates, m. p. 213° (Found : N, 15·0. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

3 : 5 : 3′ : 5′-*Tetranitrobenzil* (IV).—3 : 3′-Dinitrobenzil is so easily nitrated that the action, unless carefully controlled, may become very violent.

A solution of 10 g. of 3 : 3′-dinitrobenzil in 72 g. of concentrated sulphuric acid was heated to 100° and 60 g. of nitric acid (*d* 1·5) were slowly added, the temperature being kept between 100° and 110°. The mixture was then heated on a water-bath for a few hours, cooled, and poured over crushed ice. The yellow, viscid mass that separated was boiled repeatedly with water to extract the considerable amount of 3 : 5-dinitrobenzoic acid which it contained. The brittle, yellow, crystalline mass melting at about 174° thus obtained was practically pure 3 : 5 : 3′ : *5′-tetranitrobenzil*, the amount being about one-third of the weight of 3 : 3′-dinitrobenzil used. The aqueous extracts on condensation yielded 3 : 5-dinitrobenzoic acid, m. p. 205°, identical with the dinitrobenzoic acid obtained by nitrating *m*-nitrobenzoic acid (*Z. Chem.*, 1870, 641) and giving no depression of melting point when mixed with it.

3 : 5 : 3′ : 5′-Tetranitrobenzil is sparingly soluble in boiling alcohol and benzene, moderately easily soluble in boiling acetic acid, and separates from these solvents in bright yellow, six-sided, rhombic prisms, m. p. 179° (Found : C, 42·8 ; H, 1·7 ; N, 14·4. $C_{14}H_6O_{10}N_4$ requires C, 43·1 ; H, 1·5 ; N, 14·4%).

Oxidation of 3 : 5 : 3′ : *5′-Tetranitrobenzil.*—A solution of 1 g. of 3 : 5 : 3′ : 5′-tetranitrobenzil in 50 c.c. of boiling acetic acid was gradually treated with 0·5 g. of chromium trioxide and boiled gently for a few minutes ; the excess of chromic acid was then reduced with alcohol, and the whole evaporated to small bulk. Addition of hot dilute caustic soda solution in slight excess, filtration, and acidification of the filtrate gave 0·85 g. of 3 : 5-dinitrobenzoic acid, m. p. 205° ; a further 0·12 g. was obtained from the mother-liquor (total yield, 87% of the theoretical).

3 : 5 : 3′ : *5′-Tetranitrobenzil monophenylhydrazone*,

$$C_6H_3(NO_2)_2{\cdot}C(:N{\cdot}NHPh){\cdot}CO{\cdot}C_6H_3(NO_2)_2,$$

is produced when equivalent amounts of the tetranitrobenzil and phenylhydrazine are heated together in alcohol. It is very sparingly soluble in boiling alcohol and benzene, but more soluble in boiling acetic acid, from which it separates in small, yellow, rhombic crystals, m. p. 236° (Found : N, 17·4. $C_{20}H_{12}O_9N_6$ requires N, 17·5%).

Boiling the tetranitrobenzil for a long time with an excess of phenylhydrazine, either alone or in alcohol or acetic acid, or in acetic acid with phosphorus pentoxide, does not produce an osazone.

2 : 3-*Di*(3′ : *5′-dinitrophenyl*)*quinoxaline* separates when equivalent amounts of *o*-phenylenediamine and 3 : 5 : 3′ : 5′-tetranitrobenzil are heated together in acetic acid solution. It is slightly soluble in boiling acetic acid and separates in short, irregular, colourless prisms which contain 1 mol. of acetic acid. This is lost by drying on the water-bath (Found : loss at 110°, 11·3. Calc. : loss, 11·5%), and the crystals become opaque and melt at 285° (Found : N, 18·5. $C_{20}H_{10}O_8N_6$ requires N, 18·2%).

THE QUEEN'S COLLEGE, OXFORD. *[Received, December 29th, 1926.]*

LXXXVIII.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part IX. 2 : 3- and 2 : 5-Dinitro-4-methoxytoluenes.*

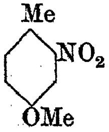
By HERBERT ERIC DADSWELL and JAMES KENNER.

IN an earlier paper (Kenner, Tod, and Witham, J., 1925, **127**, 2343), the behaviour of 4-chloro-2 : 3- and -2 : 5-dinitrotoluenes towards ammonia and sodium methoxide was examined, with the object of comparing the influences of the methyl group and the chlorine atom on the reactivities of the nitro-groups.

A similar comparison of the methyl and methoxyl groups has now been made by a study of 2 : 3- (II) and 2 : 5- (III) dinitro-4-methoxytoluenes.

It was stated by Kaufler and Wenzel (*Ber.*, 1901, **34**, 2238) that the former of these compounds is the main product of the nitration of 2-nitro-4-methoxytoluene (I), but a repetition of their work, whilst confirming the formation of this compound, showed that they had not obtained it in a pure condition, and that the 2 : 5-isomeride also can be isolated from the products of the reaction. The separation is, however, tedious and wasteful, and the ethers are more accessible from 2 : 3- and 2 : 5-*dinitro*-p-*cresols*. These are produced approximately in the proportion of 2 : 1 when 2-nitro-*p*-cresol is nitrated, and are comparatively easily separated. These results are of interest as illustrating the general tendency, emphasised by Jones and Robinson (J., 1917, **111**, 907; compare Rây and Robinson, J., 1925, **127**, 1608), for the entering group in such cases to take up the 3-position, ortho- to the nitro-group. As in the cases of the dimethyl ether of 2-nitroquinol and of 2-nitroaceto-*p*-toluidide (Page and Heasman, J., 1923, **123**, 3240; Scott and Robinson, J., 1922, **121**, 844), however, this does not occur to the entire exclusion of substitution in the 5-position. Conversely, we have found that the conditions prescribed by Scott and Robinson (*loc. cit.*) for the preparation of 2 : 5-dinitroaceto-*p*-toluidide also lead to the production of some of the 2 : 3-isomeride.

(I.)



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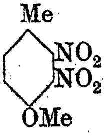

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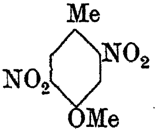
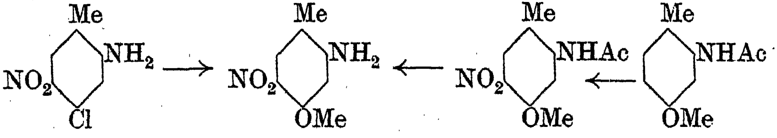


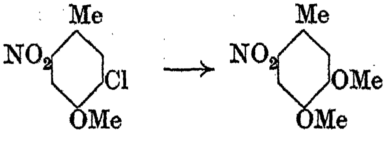
A study of the action of methyl-alcoholic ammonia on 2 : 5-dinitro-4-methoxytoluene led to no result useful for the present purpose, for most of the material was recovered unchanged after treatment at 140°, and at 150° it was converted into a mixture consisting partly of black insoluble material, from which neither of the expected toluidines could be obtained. Of these, 5-*nitro*-4-*methoxy*-o-*toluidine* (IV) was obtained by the action of sodium methoxide on 4-chloro-5-nitro-*o*-toluidine (Kenner, Tod, and Witham, *loc. cit.*), and its acetyl derivative was the sole product isolated from the nitration of 4-methoxyaceto-*o*-toluidide :



(IV.)

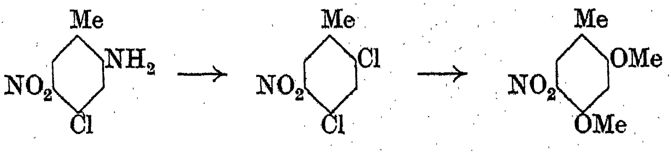
Similarly, 4-methoxyaceto-*m*-toluidide was converted by each of the methods of nitration employed solely into 6-nitro-4-methoxy-aceto-*m*-toluidide (compare Limpach, *Ber.*, 1899, **22**, 790). These results are in interesting contrast to the behaviour of the corresponding chloro-compounds, from each of which both the possible isomerides are obtained (Kenner, Tod, and Witham, *loc. cit.*).

Of the possible products of the action of sodium methoxide on the above dinitro-compound, 6-nitrohomoveratrole (V) was already known (Cousin, *Ann. Chim. Phys.*, 1898, **13**, 480; Kostanecki and Paul, *Ber.*, 1902, **35**, 2608; Gilbody and W. H. Perkin, J., 1902, **81**, 1040), and has now been prepared from 3-*chloro*-6-*nitro*-4-*methoxytoluene* (de Vries, *Rec. trav. chim.*, 1909, **28**, 401) through the agency of sodium methoxide :



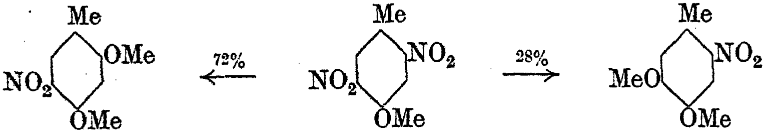
(V.)

In the same way, 5-*nitro*-2 : 4-*dimethoxytoluene* (VI) resulted from 2 : 4-*dichloro*-5-*nitrotoluene*, derived from 4-chloro-5-nitro-*o*-toluidine (Kenner, Tod, and Witham, *loc. cit.*) :

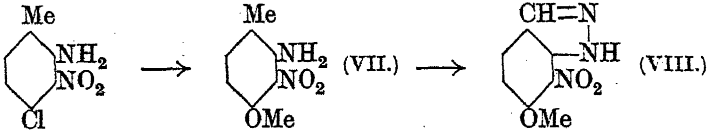


(VI.)

The 2:4-dimethoxy-derivative (VI) was also isolated from the mixture of methoxy-derivatives obtained by the action of sodium methoxide on 2 : 5-dinitro-4-methoxytoluene. This indication that displacement of the 2 predominates over that of the 5 nitro group in this reaction was confirmed by thermal analysis, which showed that the two products are formed in the ratio 72 : 28.

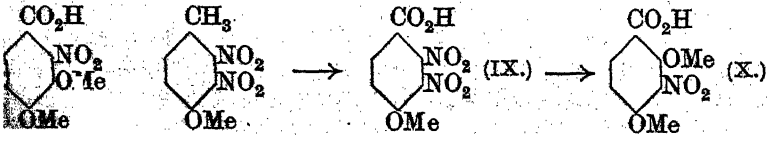


Preliminary to the study of the action of ammonia on 2 : 3-dinitro-4-methoxytoluene, *3-nitro-4-methoxy-*o*-toluidine* (VII) was prepared from 4-chloro-3-nitro-*o*-toluidine by treatment with sodium methoxide, and shown to be convertible in excellent yield into 7-nitro-6-methoxyindazole (VIII) :



(VII.) (VIII.)

Application of this reaction to the oily mixture of bases obtained from the dinitro-compound indicated that it consisted to the extent of 30% of the *o*-toluidine. In general confirmation of this result, it was possible to isolate from the mixture a base, different from the *o*-toluidine but isomeric with it, which was therefore *2-nitro-4-methoxy-*m*-toluidine*. Attempts were made by a variety of methods to prepare this base from 4-methoxy-*m*-toluidine, but without success. Both it and its isomeride could obviously be converted into the corresponding nitrodimethoxytoluenes—a point of importance in view of the interest recently evinced in the preparation of 2-nitrohomoveratrole (Merck, D.R.-P. 415315; Oberlin, *Arch. Pharm.*, 1925, **263**, 641; Gulland and Robinson, J., 1926, 1976). This was, however, deemed to be unnecessary for the present investigation, since the mixture of dimethoxynitrotoluenes arising from the action of sodium methoxide on 2 : 3-dinitro-4-methoxytoluene was an oil which offered no prospect of being separable into its components by fractional distillation. But its composition followed from its oxidation to a mixture of nitrodimethoxybenzoic acids, in which 2-nitroveratric acid (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3409) predominated. The isomeric *3-nitro-2 : 4-dimethoxybenzoic acid* (X) resulted from the action of sodium methoxide on *2 : 3-dinitro-4-methoxybenzoic acid* (IX), which in turn was prepared from 2 : 3-dinitro-4-methoxytoluene.



(IX.) (X.)

It thus appears that both ammonia and sodium methoxide displace the 3- rather than the 2-nitro-group of 2 : 3-dinitro-4-methoxytoluene, but that the 2-position of the 2 : 5-isomeride is the more liable to attack. No discrepancy of this kind was observed between the chlorodinitrotoluenes, and it will therefore be of interest to examine the behaviour of 4 : 5-dinitro-2-methoxytoluene.

EXPERIMENTAL.

Nitration of 2-*Nitro*-4-*methoxytoluene.*—The quality of the fuming nitric acid available rendered it necessary slightly to modify the conditions used by Kaufler and Wenzel (*loc. cit.*).

Sulphuric acid (60 c.c.) was gradually added to a solution of 2-nitro-4-methoxytoluene (10 g.) in glacial acetic acid (100 c.c.) and nitric acid (*d* 1·49; 40 c.c.) below 5°. The product (12 g.), after prolonged and careful fractional crystallisation from methyl alcohol, yielded 4 g. of material, m. p. 132—133° (Found: N,* 13·2%) as compared with 126—128° recorded by Kaufler and Wenzel for 2 : 3-dinitro-4-methoxytoluene. The identity of the product was proved by its reduction to the diamine, m. p. 75—76° (Kaufler and Wenzel give 72—73°), which was further characterised by condensation with benzil. 8-*Methoxy*-2 : 3-*diphenyl*-5-*methylquinoxaline* separates from acetic acid in fine, grey needles, m. p. 196—197° (Found: N, 9·15. $C_{22}H_{18}N_2$ requires N, 9·0%).

2 : 5-Dinitro-4-methoxytoluene (0·5 g.) was isolated from the mother-liquors of the above crystallisation and crystallised from benzene–light petroleum in yellow needles, m. p. 123—124° (Found: N, 13·4. Calc.: N, 13·2%). The compound had been previously prepared by G. M. Robinson (J., 1916, **109**, 1089), who found it to melt at 126°. Its orientation was proved by its reduction to a diamine, m. p. 164°, and direct comparison of this with authentic 3 : 6-diamino-4-methoxytoluene from 6-nitro-4-methoxy-*m*-toluidine (Limpach, *Ber.*, 1889, **22**, 791). Further, when a suspension of this base (5·75 g.) in crushed ice (187 g.) was oxidised by shaking it for 20 hours with the paste prepared from potassium persulphate (25 g.) and sulphuric acid (50 g.), the crude nitroso-compound obtained (4·2 g.) furnished 2 : 5-dinitro-4-methoxytoluene (2 g.), m. p. 123—124°, on oxidation at 40—50° with nitric acid (*d* 1·48; 15 c.c.).

Nitration of 2-*Nitro*-p-*cresol.*—When a mixture of glacial acetic acid (20 c.c.) and nitric acid (*d* 1·49; 16 c.c.) was added to a solution of 2-nitro-*p*-cresol (40 g.) in glacial acetic acid (160 c.c.) at 18—25°, crystalline material (18 g., m. p. 154—156°) gradually separated. The material (25 g.) precipitated on dilution of the liquor yielded another product (8 g., m. p. 112—113°) by crystallisation from alcohol, 13 g. of material being recovered from the solution. By crystallisation from glacial acetic acid, this furnished 6 g., m. p. 156—157°.

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* Determinations marked with an asterisk were carried out by Pregl's micro-Dumas procedure.

The less fusible product was 2:3-*dinitro*-p-*cresol*, which crystallised from glacial acetic acid in light yellow plates, m. p. 157—158° (Found: N, 14·1. $C_7H_6O_5N_2$ requires N, 14·1%), and was converted, by treatment in alkaline solution at 40—50° with methyl sulphate, into 2 : 3-dinitro-4-methoxytoluene, m. p. 132—133°. The lower-melting product, light brown needles, m. p. 112—113°, was 2 : 5-*dinitro*-p-*cresol* (Found: N, 14·2. $C_7H_6O_5N_2$ requires N, 14·1%), since it furnished 2 : 5-dinitro-4-methoxytoluene, m. p. 123—124°, on alkylation with methyl sulphate.

The possibility of utilising 2 : 5-dinitro-*p*-toluidine as a source of the cresol was also examined, but abandoned when it was found that the material prepared according to the directions of Scott and Robinson (*loc. cit.*) was a mixture. From 4 g. of the crude base, 1 g. of almost pure 2 : 5-dinitro-*p*-toluidine, m. p. 186—187°, was obtained by crystallisation first from alcohol and then from benzene. By crystallising the material recovered from the mother-liquors twice from methyl alcohol, 2 : 3-dinitro-*p*-toluidine (0·75 g.), m. p. 122—123°, was obtained; it was identified by comparison with an authentic specimen. The remaining material was a mixture of the isomerides.

5-*Nitro-4-methoxy*-o-*toluidine* was obtained in quantitative yield when 4-chloro-5-nitro-*o*-toluidine (2·7 g.) was heated for 6 hours at 130° with a solution of sodium (0·3 g.) in methyl alcohol (12 c.c.). It separated from methyl alcohol in light purple prisms, m. p. 158—159°, which darkened rapidly on exposure (Found: N, 15·6. $C_8H_{10}O_3N_2$ requires N, 15·4%). It was converted by reduction into the *p*-diamine, m. p. 163°, already mentioned, and furnished an *acetyl* derivative which separated from alcohol in needles, m. p. 154—155° (Found: N, 12·8. $C_{10}H_{12}O_4N_2$ requires N, 12·5%). This compound was also produced apparently as sole product when a solution of 4-methoxyaceto-*o*-toluidide (10 g.) in glacial acetic acid (15 c.c.) and sulphuric acid (20 c.c.) was treated at 15—20° with nitric acid (*d* 1·49; 3 c.c.). It was conveniently hydrolysed in 1 hour by boiling it with 50% sulphuric acid. Attempts to obtain an indazole derivative from the base (compare 3-nitro-4-methoxy-*o*-toluidine, later) were unsuccessful.

6-Nitro-4-methoxyaceto-*m*-toluidide was prepared by Limpach (*loc. cit.*) from 4-methoxyaceto-*m*-toluidide. The nitration was repeated under various conditions which, in the case of acetanilide, are known to favour ortho-nitration: (1) a suspension of the acetotoluidide (21·6 g.) in acetic anhydride (20 c.c.) was treated at 10—20° with a mixture of nitric acid (*d* 1·48; 10 g.), urea (0·2 g.), and acetic anhydride (6 g.); (2) nitric acid (*d* 1·48; 3 c.c.) was added to a solution of the acetotoluidide (11 g.) in glacial acetic acid (15 c.c.) and sulphuric acid (20 c.c.) at 10—15°; (3) a solution of 4-methoxy-*m*-toluidine (5·5 g.) in acetic anhydride (6 c.c.) was added at 40—50° to a mixture of cupric nitrate (5 g.) and acetic anhydride (15 c.c.) (compare Menke, *Rec. trav. chim.*, 1925, **44**, 141). In every case a large proportion of the pure acetyl derivative was at once obtained, whilst hydrolysis of material recovered from the crystallisation liquors furnished the corresponding amine, with no evidence of its isomeride.

4-*Methoxy*-m-*oxalotoluidide*, from 4-methoxy-*m*-toluidine and ethyl oxalate, was precipitated from methyl-alcoholic solution by addition of chloroform in needles, m. p. 218° (Found: N, 8·7. $C_{18}H_{20}O_4N_2$ requires N, 8·5%). Attempts to use this for the preparation of 2-nitro-4-methoxy-*m*-toluidine (compare Hadfield and Kenner, P., 1914, 253) were also unsuccessful.

2 : 4-*Dichloro*-5-*nitrotoluene*, prepared from 4-chloro-5-nitro-*o*-toluidine by the usual procedure, crystallised from alcohol in needles, m. p. 49—50° (Found: N, 6·7. $C_7H_5O_2NCl_2$ requires N, 6·8%).

5-*Nitro*-2 : 4-*dimethoxytoluene* was produced when 2 : 4-dichloro-5-nitrotoluene (4 g.) was heated for 6 hours at 115—120° with a solution of sodium (0·8 g.) in methyl alcohol (32 c.c.). It separated from light petroleum in yellow needles, m. p. 117—118° (Found: N, 7·4. $C_9H_{11}O_4N$ requires N, 7·1%).

3-*Chloro*-6-*nitro*-4-*methoxytoluene*, from 6-nitro-4-methoxy-*m*-toluidine, crystallised from alcohol in needles, m. p. 94—95° (Found: N,* 7·1. $C_8H_8O_3NCl$ requires N, 6·95%). It was converted in 6 hours by methyl-alcoholic sodium methoxide at 115—120° into 6-nitro-3 : 4-dimethoxytoluene, m. p. 119—120° (Found: N, 7·2%). De Vries (*loc. cit.*) gives 94° as the melting point.

Action of Sodium Methoxide on 2 : 5-*Dinitro*-4-*methoxytoluene*.—When the dinitro-compound (1·5 g.) was heated with a boiling solution of sodium (0·15 g.) in methyl alcohol (6 c.c.), neutrality was attained after 5 hours. The product, after four crystallisations from light petroleum (b. p. 80—110°), yielded 5-nitro-2 : 4-dimethoxytoluene (0·2 g.), m. p. 116—117°, which did not depress the melting point of an authentic specimen. In order to ascertain the actual proportion of this and its isomeride formed in the reaction, the product from another similar operation was isolated and dried in the usual manner. It solidified at 90·6°, and after the addition of 0·28 g. to 1·2 g. of the material, the solidifying point was 96°. A series of determinations of the temperatures of solidification of mixtures of the two isomerides yielded the following results (*a* is the percentage of 6-nitro-3 - 4-dimethoxytoluene):

a.	100	91·8	83·2	76·3	66·5	60·7	55·7	54·3	51·5	51·2
s.p.	115·5°	110·6°	105·5°	100·2°	90·7°	83·0°	78·6°	77·7°	77·6°	78·2°
a.	50·0	48·3	47·8	47·3	44·9	41·6	38·8	31·4	25·3	19·3
s.p.	78·8°	78·0°	77·6°	77·2°	79·2°	81·7°	82·8°	87·6°	93·2°	98·6°
a.	10·2	0								
s.p.	105·2°	113°								

From these it appears that the two isomerides combine in molecular proportion, and that the above-mentioned mixture contained 72% of 5-nitro-2 : 4-dimethoxytoluene.

3-*Nitro*-4-*methoxy*-o-*toluidine* was prepared by heating 4-chloro-3-nitro-*o*-toluidine (4·1 g.) for 6 hours at 125—130° with a solution of sodium (0·46 g.) in methyl alcohol (18·2 c.c.). The mixture was then neutral and yielded a product, which crystallised from dilute methyl alcohol in yellow needles, m. p. 61—62°. This was free from halogen and depressed the melting point of the original chloro-compound (Found: N,* 15·3. $C_8H_{10}O_3N_2$ requires N, 15·4%). Its *acetyl* derivative crystallised from benzene in needles, m. p. 176—176·5° (Found: N,* 12·6. $C_{10}H_{12}O_4N_2$ requires N, 12·5%). A solution of the base (0·5 g.) in glacial acetic acid (50 c.c.) which had been treated at 0° with a solution of sodium nitrite (2*N*; 3·4 c.c.) deposited a brownish-red precipitate after 48 hours. The product (0·44 g.), isolated by extracting the mixture with benzene, crystallised from alcohol in fine, red needles, m. p. 173—174°. Analysis showed it to be 7-*nitro*-6-*methoxyindazole* (Found: N,* 21·3. $C_8H_7O_3N_3$ requires N, 21·8%).

Action of Methyl-alcoholic Ammonia on 2 : 3-*Dinitro*-4-*methoxytoluene*.—Four separate quantities of the dinitro-compound (2·1 g.) were each treated with methyl alcohol (27 c.c.) and ammonium hydroxide (*d* 0·880; 5 c.c.) at 145—150° for 7 hours. The residue after removal of methyl alcohol by distillation was extracted with hot concentrated hydrochloric acid (400 c.c.) in order to separate unchanged material (0·5 g.) from the basic product (6·8 g.), which was recovered from the acid solution in the usual manner. When a portion of this (1·3 g.) was dissolved in glacial acetic acid (66 c.c.) and treated at 0° with sodium nitrite solution (4·5 c.c.), it yielded crude 7-nitro-6-methoxyindazole (0·35 g.), which crystallised from alcohol in red needles, m. p. 165—166°, and was identified by comparison with the authentic compound. The yield of indazole, in comparison with that attained in the preparation described above, indicated the presence of 30% of 3-nitro-4-methoxy-*o*-toluidine in the basic mixture. When a further quantity (4 g.) of this was repeatedly extracted with hot light petroleum (b. p. 40—60°), a red solid was obtained. By crystallisation from methyl alcohol, this was obtained in orange needles (0·7 g.), m. p. 49—50° (Found : N,* 15·5. $C_8H_{10}O_3N_2$ requires N, 15·4%). Since the compound depressed the melting point of authentic 3-nitro-4-methoxy-*o*-toluidine, it was *2-nitro-4-methoxy-*m*-toluidine*. Its *acetyl* derivative (Found : N,* 12·3. $C_{10}H_{12}O_4N_2$ requires N, 12·5%) crystallised from benzene in small, white needles, m. p. 170—171°, and depressed the melting point of 3-nitro-4-methoxyaceto-*o*-toluidide.

When 2 : 5-dinitrotoluene (8·4 g.) was treated in the same manner for 14 hours at 150—160°, there were obtained a black deposit (0·65 g.), unchanged material (1 g.), and red semi-solid material (2 g.), precipitated from dilute mineral acid solution, and an oily mixture of bases (2·5 g.), which furnished a semi-solid acetyl derivative.

2 : 3-*Dinitro-4-methoxybenzoic acid* was prepared by boiling a mixture of 2 : 3-dinitro-4-methoxytoluene (10 g.) with a solution of potassium permanganate (20 g.) and magnesium sulphate (15·6 g.) in water (900 c.c.) for 4 hours. Unchanged dinitro-compound (4 g.) was recovered, and the acid (4·9 g.) isolated in the usual manner. It crystallised from water in needles, m. p. 248—250° (decomp.) (Found : N, 11·8; equiv., 243·6. $C_8H_6O_7N_2$ requires N, 11·6%; equiv., 242). The *methyl* ester separated from methyl alcohol in needles, m. p. 156° (Found : N, 11·1. $C_9H_8O_7N_2$ requires N, 10·9%). A solution of the acid (1 g.) in methyl alcohol (15 c.c.) was heated with a solution of sodium (0·2 g.) in methyl alcohol (12 c.c.) for 14 hours at 120°; the resulting neutral solution furnished *3-nitro-2 : 4-dimethoxybenzoic acid* (0·75 g.) on acidification. This crystallised from water in needles, m. p. 210—212° (Found : N,* 6·4; equiv., 225·7. $C_9H_9O_6N$ requires N, 6·1%; equiv., 227). The *methyl* ester crystallised from methyl alcohol in large prisms, m. p. 118—119° (Found : N,* 6·0. $C_{10}H_{11}O_6N$ requires N, 5·8%). The acid and its ester were shown by direct comparison to be distinct from authentic 2-nitroveratric acid, m. p. 201—202°, and its methyl ester, m. p. 127—128° (Pschorr and Sumuleanu, *loc. cit.*).

Action of Sodium Methoxide on 2 : 3-Dinitro-4-methoxytoluene.—Whether the dinitro-compound (3 g.) was heated with a solution of sodium (0·3 g.) in methyl alcohol (12 c.c.) for 8 hours at 125° or for 20 hours at 110—115°, a quantity remained unchanged and crystallised when the solution was concentrated. When the residues from a number of such experiments were fractionated, a mixture of nitrodimethoxytoluenes passed over at 132—136°/2 mm., leaving a further quantity of dinitromethoxytoluene behind. The distillate (6 g.) was completely oxidised in 4 hours by a boiling, mechanically agitated solution of potassium permanganate (16 g.) in water (800 c.c.).

The acid so obtained (4·5 g.) crystallised from water in needles, m. p. 172—177° (Found : equiv., 223·2), and on esterification furnished a mixture of methyl esters, m. p. 105—110°, from which methyl 2-nitroveratrate, m. p. 125—126°, was separated by recrystallisation from methyl alcohol. Its identity was established by direct comparison with an authentic specimen, and it was similarly shown to be distinct from methyl 3-nitro-2 : 4-dimethoxybenzoate.

THE UNIVERSITY, SYDNEY. [*Received, December 29th,* 1926.]

LXXXIX.—*Melezitose and Turanose.*

By GRACE CUMMING LEITCH.

THE discovery by Hudson and Sherwood (*J. Amer. Chem. Soc.*, 1918, **40**, 1456) that the manna found adhering to the twigs and needles of the Douglas fir consists largely of melezitose has made it possible to obtain this trisaccharide in a pure condition, and Harding (*Sugar*, 1923, 240) has shown how best to isolate the sugar from this source.

As the elucidation of the structure of this trisaccharide would solve simultaneously the problem of the structure of the reducing disaccharide turanose, an investigation was carried out by the methylation method. The conclusion was drawn that melezitose consists of two glucose residues of amylene-oxidic type united with one fructose residue of the type found in sucrose. While research on the nature of the fructose derivative was proceeding, two papers on the same topic were published by Zemplén and Braun (*Ber.*, 1926, **59**, 2230, 2539), who have arrived at a similar conclusion. Since the experimental method hereafter described differs from that of Zemplén, and since, in addition, proof is given that the fructose residue contains an oxide linking similar to that in sucrose, it was considered advisable to submit the following confirmatory evidence with regard to the nature of these two sugars.

Methylation of melezitose by the usual method with methyl sulphate and sodium hydroxide gave *hendecamethyl melezitose*, a thick syrup which could be distilled under a high vacuum. On hydrolysis with hydrochloric acid sufficiently concentrated to rupture completely the methylated trisaccharide, this syrup yielded amylene-oxidic tetramethyl glucose and trimethyl γ-fructose in the proportion 2 : 1.

Conditions of hydrolysis similar to, but slightly more drastic than, those used by Tanret (*Compt. rend.*, 1906, **142**, 1424) for the partial hydrolysis of the unsubstituted sugar into turanose and glucose were also employed. A pure methylated turanose, however, could not be thus obtained, for scarcely any change in rotation took place as hydrolysis proceeded and therefore polarimetric observations were of little avail for detecting its completion. Tanret's method was therefore abandoned, since, during hydrolysis with hydrochloric acid, no such difficulty was encountered, and the products could be separated from each other in a pure condition by extraction of the solution with chloroform after neutralisation with barium carbonate.

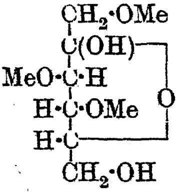
Most of the trimethyl γ-fructose remained in the aqueous solution, but some of it, together with the tetramethyl glucose, was dissolved by the chloroform. As this does not take place in the separation of tetra- and tri-methyl glucoses (Irvine and Black, J., 1926, 862; Cooper, Haworth, and Peat, *ibid.*, p. 876), the conclusion is drawn that the presence of tetramethyl glucose in an aqueous solution induces extraction of some of the trimethyl γ-fructose by chloroform, although the latter has no solvent effect on trimethyl glucose under the special conditions of the experiments. This may be due to the fact that in the one case a derivative of a γ-sugar is under investigation, whilst in the other both the tetra- and the tri-methyl glucose are of the stable or amylene-oxidic type.

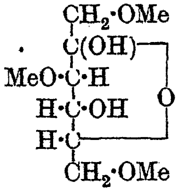
On concentration of the chloroform extract, tetramethyl glucose of the stable or amylene-oxidic type was isolated. The trimethyl fraction which remained in the aqueous solution was proved to be a ketose by the deep red coloration which it imparted to Seliwanoff's reagent (resorcinol and hydrochloric acid). It readily reduced Fehling's solution and decolorised neutral potassium permanganate in the cold. $[\alpha]_D$ in absolute ethyl alcohol, $+ 55{\cdot}5°$ (Zemplén and Braun record $[\alpha]_D + 24°$).

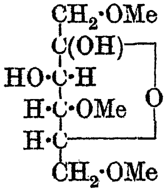
Zemplén and Braun apparently assumed that the fructose fragment of melezitose contains the same type of oxide linking as is present in the fructose of inulin and sucrose. It was obviously necessary to prove this, and the trimethyl fructose was therefore methylated with silver oxide and methyl iodide; the mobile syrup (n_D 1·4445) thus obtained gave, as the sole product of hydrolysis, a reducing sugar which agreed in physical constants with the tetramethyl γ-fructose resulting from the hydrolysis of octa- or hepta-methyl sucrose (Haworth, J., 1920, **117**, 199). This precluded the possibility of the comparatively high specific rotation of the trimethyl fructose being due to traces of tetramethyl glucose.

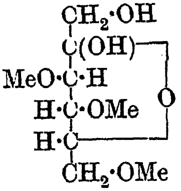
Account being taken of the recent arguments of Haworth and

Hirst (J., 1926, 1858) regarding the structure of γ-fructose derivatives, the four trimethyl γ-fructoses are :


(I.)


(II.)

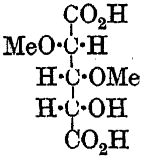

(III.)


(IV.)

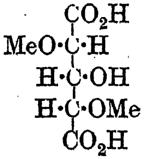
Of these, (IV) is ruled out, since turanose is capable of forming an osazone (Fischer, *Ber.*, 1894, **27**, 2486). The hydroxyl in the position next the ketose group cannot therefore be engaged in a biose linking, whence it follows that it must be methylated in the fructose fragment. In the early experiments carried out by the author, the trimethyl fructose was distilled before being analysed; the yield of trimethyl fructose which distilled was not good, and a certain proportion invariably remained as a non-volatile residue. The methoxy-content varied between 42% and 45% (Calc. for trimethyl fructose, 41·9%; for trimethoxy-anhydro-hexose, 45%). As the trimethyl fructose can be isolated in a pure condition without distillation, as seen above, this method was abandoned, but it was useful in having supplied a clue to the structure of the trimethyl fructose component. It appeared probable that distillation had resulted in the elimination of a molecule of water with consequent formation of an anhydro-fructose derivative. Anhydride formation is known to take place in 2 : 3 : 4-trimethyl glucose (Irvine and Oldham, J., 1921, **119**, 1744), which is partly converted into trimethyl glucosan on distillation. Comparison of rotation values is therefore not a trustworthy means of settling the identity of the substances under investigation, since one specimen may exist as the free sugar derivative and the other may be partly converted into an anhydro-sugar derivative.

Substances having formulæ (III) and (IV) would, on formation of anhydro-fructose derivatives, yield substances containing an ethylene-oxide linking, whilst in the product from (II) there would be present a propylene-oxide ring. No positive evidence of the existence of either of these two types of ring compounds in methylated fructose derivatives is found in the literature, whilst Haworth and Hirst (*loc. cit.*) have definitely proved that an amylene-oxide ring exists in the normal or stable type of fructose. Anhydride formation is therefore most likely where the formation of an oxide ring of this type is possible. Formula (I) admits of this, and therefore, in all probability, represents the trimethyl fructose obtained from methylated melezitose. This deduction agrees with the experimental results of Zemplén and Braun quoted below. These authors have ruled out (III) on the ground that the reduction product of trimethyl fructose shows no alteration in rotation on addition of boric acid and therefore cannot have vicinal free hydroxy-groups. They have ascribed to trimethyl fructose formula (I), since they obtained from it by oxidation a hydroxydimethoxyglutaric acid (V) which was not identical with authentic β-hydroxy-αα′-dimethoxyglutaric acid (VI) obtained by them by other means.

(V.)



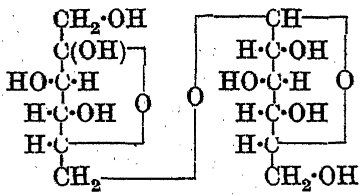
$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{MeO{\cdot}C{\cdot}H} \\ | \\ \mathrm{H{\cdot}C{\cdot}OMe} \\ | \\ \mathrm{H{\cdot}C{\cdot}OH} \\ | \\ \mathrm{CO_2H} \end{array}$$



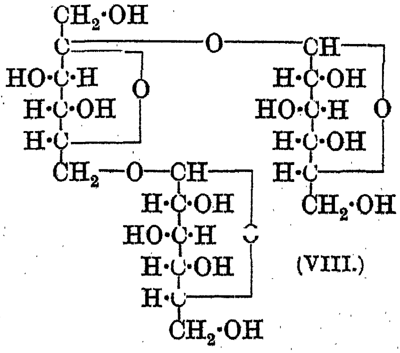
$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{MeO{\cdot}C{\cdot}H} \\ | \\ \mathrm{H{\cdot}C{\cdot}OH} \\ | \\ \mathrm{H{\cdot}C{\cdot}OMe} \\ | \\ \mathrm{CO_2H} \end{array}$$

(VI.)

Turanose must therefore be represented by (VII) and melezitose by (VIII).



(VII.)



(VIII.)

EXPERIMENTAL.

Methylation of Melezitose. Isolation of Hendecamethyl Melezitose.—(The melezitose used in the following operations was supplied by Messrs. Baird and Tatlock, agents for The Digestive Ferments Co., Detroit, Mich., U.S.A.) Melezitose (25 g.), dissolved in the minimum volume of water, was methylated at 70° in the usual way (Haworth, J., 1915, **107**, 11) with 80 c.c. of methyl sulphate and 80 g. of 30% aqueous sodium hydroxide, care being taken to avoid acidity. The mixture was finally raised to 100° during the last half-hour of the methylation. Extraction with chloroform yielded a partly methylated syrup, which was again methylated, half-quantities of the methylating reagents being used. The chloroform extract (24 g.) was remethylated four times by Purdie's method, with excess of silver oxide and methyl iodide, 24 g. of syrup being again obtained. This material was distilled in the vacuum of a Gaede pump; 19·5 g., b. p. 236°/0·01 mm., were then obtained [Found: OMe, 49·7; C, 52·7; H, 8·2. $C_{18}H_{21}O_5(OMe)_{11}$ requires OMe, 51·8; C, 52·9; H, 8·2%]. The distillate had n_D 1·4680, and $[\alpha]_D + 114°$ in methyl alcohol (*c*, 0·85) and + 108·6° in ethyl alcohol (*c*, 2·2). These results agree with Zemplén and Braun's $[\alpha]_D + 113·4°$ in alcohol.

Hydrolysis of Hendecamethyl Melezitose.—Method 1. This method, which was afterwards abandoned in favour of method (2) for the reason already given, consisted in applying conditions of hydrolysis similar to those employed by Tanret (*loc. cit.*) for the graded rupture of the hendecamethyl melezitose into a substituted hexose fraction and a methylated disaccharide fraction.

8 G. of an 8% solution of hendecamethyl melezitose in 20% acetic acid were hydrolysed by heating for 2 hours at 95°, the specific rotation changing from + 101·2° to + 102°. Further heating for 1 hour at 110° resulted in a further change in rotation to $[\alpha]_D + 103·6°$. Chloroform then extracted from the mixture, neutralised by barium carbonate, 7·25 g. of a reducing syrup (n_D 1·4650). Evaporation of the aqueous solution to dryness and subsequent digestion of the barium acetate with chloroform gave no further syrup. From solubility considerations, the syrup was therefore not expected to contain any trimethyl hexose. (Tetramethyl glucose and heptamethyl turanose would both be extracted from aqueous solution by chloroform.) Distillation of the syrup remaining after removal of the chloroform gave two fractions: (1) b. p. 115°/0·3 mm. This fraction crystallised at once and was identified as tetramethyl glucose; (2) b. p. 185—190°/0·2 mm., n_D 1·4652 (Found: OMe, 46·7; C, 50·4, 50·9; H, 8·4, 8·4. Calc.: OMe, 49·3; C, 51·8; H, 8·2%).

The above figures are not in agreement with those for a heptamethyl turanose, although the two analyses agree with each other. In order to discover whether this syrup would yield tetramethyl glucose and trimethyl fructose on hydrolysis, it was heated for 1 hour at 95° with 5% hydrochloric acid. The solution had then darkened considerably and the initial rotation of + 127° had changed to + 78° and was constant. Isolation of the products followed, by the method described below, and tetramethyl glucose and a trimethyl fructose were identified.

Method 2. *Isolation of tetramethyl glucose and trimethyl γ-fructose.* Hendecamethyl melezitose (10 g.) was dissolved in 5% hydrochloric acid to give an 8% solution. After 2 hours' heating at 95°, no undue darkening of the solution had taken place and the rotation had changed from the initial value + 104° to + 70° and was constant.

The solution was diluted with water, neutralised with barium carbonate, and shaken with an excess of chloroform, whereby the syrupy product was separated into a chloroform-soluble portion (A) and a water-soluble portion (B).

Treatment of A. On removal of the solvent from solution A a syrup weighing just over 6 g. was obtained. To ensure that this was a pure tetramethyl glucose uncontaminated by trimethyl hexose, the above process was repeated, by redissolving the syrup in water and shaking the solution with small volumes of chloroform. A separation into two portions was again effected, as some of the syrup (A1) was removed from the aqueous solution under these conditions whilst the rest of the syrup (A2) was extracted only when large volumes of chloroform were used.

*The portion A*1 (trimethyl γ-fructose) weighed 1·1 g., reduced Fehling's solution, gave Seliwanoff's reaction, and had n_D 1·4670 (Found: OMe, 43·0. Calc.: 41·9%). It was therefore regarded as, in the main, trimethyl fructose.

*Treatment of A*2 (tetramethyl glucose). A2 crystallised after removal of the solvent chloroform. It was drained on porous tile, and thereafter crystallised from light petroleum in long needles, m. p. 89°; mixed m. p. with authentic tetramethyl glucose, 88° (Found: OMe, 50·7. Calc.: 52·5%). It had $[\alpha]_D$ in water (c, 1·7) $+$ 91·7°, falling to $+$ 83° (equilibrium value). The substance was therefore stable amylene-oxidic tetramethyl glucose. The yield represented approximately two-thirds of the total hydrolysed material (10 g. of hendecamethyl melezitose gave, after hydrolysis, 8·7 g. of syrup, from which 4·6 g. of tetramethyl glucose and 2·3 g. of trimethyl fructose were obtained in the pure state).

Treatment of B (trimethyl γ-fructose). The aqueous solution from the hydrolysis was carefully evaporated to dryness under diminished pressure, and the residue refluxed with chloroform. This extracted a syrup (1·2 g.) (Found: OMe, 40·0. Calc.: 41·9%), n_D 1·4660, which reduced Fehling's solution very readily and instantly decolorised neutral potassium permanganate solution. On solution in cold aqueous sodium hydroxide, it immediately developed a yellow colour; on heating, this colour deepened to dark brown. Comparative tests with fructose gave the same deepening in colour, while solutions of glucose derivatives remained pale yellow even after prolonged boiling. $[\alpha]_D$ in ethyl alcohol (c, 6), $+$ 55·5°.

Methylation of Trimethyl Fructose. Isolation of Tetramethyl Methylfructoside and Tetramethyl γ-Fructose.—The trimethyl fructose was methylated with an excess of Purdie's reagents. After one methylation a non-reducing syrup (n_D 1·4445) was isolated. This was hydrolysed completely by treatment with 8% hydrochloric acid at 95° for ½ hour. From the solution, neutralised with barium carbonate, chloroform extracted a syrup which reduced Fehling's solution strongly, had n_D 1·4540, and showed the following rotations : $[\alpha]_D + 24{\cdot}4°$ in methyl alcohol (*c*, 0·9), $+ 29{\cdot}1°$ in ethyl alcohol (*c*, 4·2), $+ 32{\cdot}8°$ (permanent) in water (*c*, 3). These results are in agreement with the standard values for tetramethyl γ-fructose (Haworth, *loc. cit.*).

The author wishes to express her thanks to Dr. E. L. Hirst for the interest he has taken in the research.

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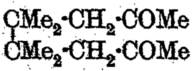
NEWCASTLE-ON-TYNE. [*Received, February 4th,* 1927.]

XC.—*Ring-chain Tautomerism. Part XVI. The Effect of Two Adjacent* gem-*Dimethyl Groups on the Ease of Formation of the* cyclo*Pentane Ring.*

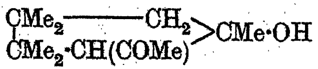
By ISRAEL VOGEL.

THE effect of the *gem*-dimethyl and other groups on the ease of formation of *cyclo*propane, *cyclo*butane, and *cyclo*pentane rings has formed the subject of numerous communications from these laboratories, but the influence of two adjacent *gem*-groups on ring formation does not appear to have been studied. The present communication deals with the effect of two adjacent *gem*-dimethyl groups on the formation of the *cyclo*pentane ring. This case is of especial interest from the point of view of the modified strain theory of Thorpe and Ingold, since the angle between the remaining two valencies of a carbon atom attached to a *gem*-dimethyl group is 109·5° (Ingold, J., 1921, **119**, 305), which differs only slightly from the angle of the normal *cyclo*pentane ring. On theoretical grounds, it would therefore be expected that in a system containing two adjacent *gem*-dimethyl groups and capable of exhibiting the phenomenon of ring-chain tautomerism, the ring isomeride would predominate; consequently the tautomerism of the substituted 1 : 6-diketone, αδ-diacetyl-ββγγ-tetramethylbutane (I), has been investigated.

(I.)



$$\begin{array}{l}\mathrm{CMe_2{\cdot}CH_2{\cdot}COMe}\\ |\\ \mathrm{CMe_2{\cdot}CH_2{\cdot}COMe}\end{array}$$



$$\left.\begin{array}{l}\mathrm{CMe_2}\text{——}\mathrm{CH_2}\\ |\\ \mathrm{CMe_2{\cdot}CH(COMe)}\end{array}\right>\mathrm{CMe{\cdot}OH}$$

(II.)

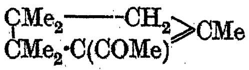
This would be expected to exist mainly in the form of the ring isomeride (II). It may be said at once that, although the mode of preparation of the compound left no doubt as to its having the open-chain formula (I) at the moment of formation, yet its properties indicated that it reacted exclusively in the form of the ring isomeride (II). No evidence could be obtained of the existence of the open-chain compound. It is noteworthy that neither αδ-diacetylbutane, $\mathrm{COMe{\cdot}[CH_2]_4{\cdot}COMe}$ (III) (Marshall and Perkin, J., 1890, **57**, 241) nor αδ-dibenzoylbutane, $\mathrm{COPh{\cdot}[CH_2]_4{\cdot}COPh}$ (IV) (Wollemann, Diss., Göttingen, 1913), the simplest 1 : 6-diketones, shows any tendency to react in the ring form as would be expected from theory. Both react exclusively as diketones, although, in common with all 1 : 6-diketones, they possess a great tendency to pass into a five-membered ring by the elimination of water (compare Kipping and Perkin, J., 1889, **55**, 330; 1890, **57**, 1, 29; 1891, **59**, 214; Kipping and Mackenzie, J., 1891, **59**, 571).

The requisite 1 : 6-diketone was prepared by the reduction of mesityl oxide by moist aluminium amalgam, the reaction following the equation

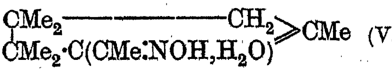
$$2C_6H_{10}O + 2H = C_{12}H_{22}O_2.$$

This reduction had been previously studied by other investigators, whose results can now be readily interpreted if (II) be taken as the formula of the reduction product. Harries and Hübner (*Annalen*, 1897, **296**, 295; compare Harries and Eschenbach, *Ber.*, 1896, **29**, 380) studied the reduction of mesityl oxide by sodium and by aluminium amalgam and assigned the constitution (V) ($C_{12}H_{20}O$) to the product, although this was not in strict accordance with the analytical results, as was first pointed out by Law (J., 1912, **101**, 1016).

(V.)



$$\left.\begin{array}{l}\mathrm{CMe_2{-}CH_2}\\ \mathrm{CMe_2{\cdot}C(COMe)}\end{array}\right>\mathrm{CMe}$$



$$\left.\begin{array}{l}\mathrm{CMe_2{-}CH_2}\\ \mathrm{CMe_2{\cdot}C(CMe{:}NOH,H_2O)}\end{array}\right>\mathrm{CMe}$$

(VI.)

They prepared two isomeric *mono*-oximes of the formula $\mathrm{C_{12}H_{20}N{\cdot}OH,H_2O}$ to which the constitution (VI) was given. Law (*loc. cit.*) effected the reduction by an electrolytic process and obtained the same products. He was, however, able to isolate a solid which he regarded as the pure reduction product ($C_{12}H_{22}O_2$), yielding a *mono*-semicarbazone, m. p. 185—186°, and a *mono*-oxime, identical with one of the oximes prepared by Harries and Hübner. Law does not assign any definite constitution to the reduction product, but merely gives the following possible constitutional formulæ:

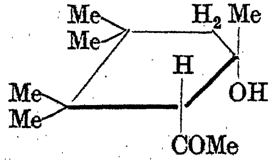
(*a*) $\mathrm{COMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CMe_2{\cdot}CH_2{\cdot}COMe}$.
(*b*) $\mathrm{CMe_2{:}CH{\cdot}CMe(OH){\cdot}CMe(OH){\cdot}CH{:}CMe_2}$.
(*c*) $\mathrm{COMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CMe(OH){\cdot}CH{:}CMe_2}$.

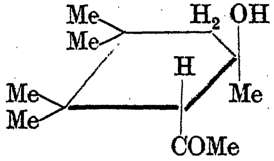
and remarks that the most probable constitution is (*c*).

The results of the author, however, are in agreement neither with the formula of Harries and Hübner nor with those of Law, but can be readily interpreted in terms of the constitution (II). Indeed, all the apparently divergent results of previous investigators can be simply explained by the new formula.

The reduction of mesityl oxide by moist aluminium amalgam resulted in the formation of a solid (α) and a liquid (β) form of the reduction product; the former passed into the latter on exposure to the atmosphere unless the oily liquid adhering to the solid was removed by recrystallisation. The solid form yielded a *mono*-semicarbazone, m. p. 185°, identical with that obtained by Law (*loc. cit.*), whilst the liquid also yielded a *mono*-semicarbazone, m. p. 165°. Further, the α-form yielded a *mono*-benzoyl derivative, m. p. 115°, the β-form a *mono*-benzoyl derivative, m. p. 42°, whilst tetramethylsuccinic acid resulted from both forms on oxidation with chromic acid. There appears to be little doubt that the solid and liquid forms are *cis*- and *trans*-modifications (VII) and (VIII), the α-form probably having the configuration (VII). The existence of two isomeric *mono*-oximes discovered by Harries and Hübner (*loc. cit.*) is in complete harmony with the above formulæ, but the constitution (VI) assigned to them by these authors must be regarded as erroneous, the correct constitutions being those represented by the oximes of the two stereoisomerides (VII) and (VIII).

(VII.)



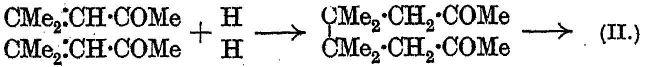


(VIII.)

The ring compound (II) is very stable towards oxidising agents. Sodium hypochlorite and potassium permanganate do not appear to have any marked effect, although with sodium hypobromite a quantitative yield of bromoform corresponding to one acetyl group was obtained, but unfortunately no other product could be isolated in sufficient quantity to admit of its complete identification. Fission of the ring took place with chromic acid and tetramethylsuccinic acid was formed.

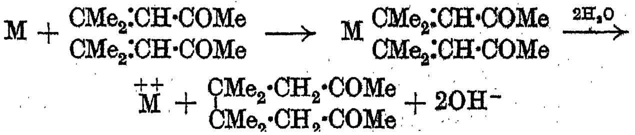
The remarkable influence which two adjacent *gem*-dimethyl groups exert on the formation of a five-membered ring is further illustrated by the fact that all attempts to prepare the anilic acid and acid chloride of tetramethylsuccinic acid have failed, the ring anil and anhydride being invariably formed (Auwers and Gardner, *Ber.*, 1890, **23**, 3622). It is apparent that experiment fully confirms the predictions made from the modified strain theory of Thorpe and Ingold and one may assert, with some confidence, that the production of an open-chain compound containing two adjacent *gem*-dimethyl groups will be practically if not entirely impossible should there be a possibility of the formation of a five-membered ring.

The scheme for the formation of the reduction product of mesityl oxide may be represented as follows (compare Law, J., 1912, **101**, 1016):



$$\begin{matrix}CMe_2{:}CH{\cdot}COMe\\ CMe_2{:}CH{\cdot}COMe\end{matrix} + \begin{matrix}H\\ H\end{matrix} \longrightarrow \begin{matrix}CMe_2{\cdot}CH_2{\cdot}COMe\\ CMe_2{\cdot}CH_2{\cdot}COMe\end{matrix} \longrightarrow \quad \text{(II.)}$$

The coupling at the β-position of reduced residues has been previously observed in the reaction between moist sodium or aluminium amalgam and benzylideneacetone (Harries and Eschenbach, *Ber.*, 1896, **29**, 380), benzylideneacetophenone, phorone (Harries and Hübner, *Annalen*, 1897, **296**, 295), and other compounds (*Ber.*, 1898, **31**, 1806; *Annalen*, 1904, **330**, 235; Möller, Diss., Rostock, 1905) and more recently by Higginbotham and Lapworth (J., 1923, **123**, 1618) in the reduction of ethyl ethylidenemalonate by moist sodium amalgam. If mesityl oxide be written $Me_2\overset{+}{C}{=}\overset{-}{C}H{-}\overset{+}{C}Me{=}\overset{-}{O}$ in accordance with the theory of alternate latent polarities, it is evident that coupling takes place between carbon atoms denoted by + signs (compare Higginbotham and Lapworth, *loc. cit.*). The author is inclined to accept the mechanism (*b*) of Higginbotham and Lapworth as that which most probably represents the course of the reaction in the reduction of mesityl oxide by moist aluminium amalgam. The modified method of reduction employed results in the presentation of a very large surface to the reacting compound and one may assume that the molecules are adsorbed on the surface of the metal and actual reaction takes place in the surface, where chemical forces are known to be very powerful, according to the scheme:



$$M + \begin{matrix}CMe_2{:}CH{\cdot}COMe\\ CMe_2{:}CH{\cdot}COMe\end{matrix} \longrightarrow M\begin{matrix}CMe_2{:}CH{\cdot}COMe\\ CMe_2{:}CH{\cdot}COMe\end{matrix} \xrightarrow{2H_2O}$$
$$\overset{++}{M} + \begin{matrix}CMe_2{\cdot}CH_2{\cdot}COMe\\ CMe_2{\cdot}CH_2{\cdot}COMe\end{matrix} + 2OH^-$$

EXPERIMENTAL.

Preparation of Aluminium Amalgam.—200 G. of thin aluminium foil in strips about 6 inches long and 1 inch wide, loosely folded, are covered with a 10% solution of sodium hydroxide and warmed until a vigorous evolution of hydrogen has taken place for several minutes. The foil is then washed with water and with rectified spirit, the latter operation producing an exceptionally clean surface for amalgamation. Sufficient of a 2% solution of mercuric chloride is added to cover the aluminium completely and is allowed to act for 2 minutes; it is then poured off and the amalgam is washed with water, with rectified spirit, and finally with moist ether. The amalgam is covered with about 3 litres of moist ether and is ready for immediate use. Repetition of the process is unnecessary, as it does not materially affect the yield of the reduction product.

*Reduction of Mesityl Oxide. Formation of 5-Acetyl-*1 : 3 : 3 : 4 : 4-*pentamethyl*cyclo*pentan-*1-*ol* (II).—Mesityl oxide (200 g.), prepared in 65% yield by the method described by Roger Adams (" Organic Syntheses," 1921, Vol. 1, p. 53), is added to the aluminium amalgam covered with moist ether in a flask fitted with two double-surface condensers. The evolution of hydrogen ceases almost immediately after the addition of the mesityl oxide and after about 20 minutes the ether boils; too vigorous ebullition must be checked by cooling the flask with running water. The reduction is usually complete after about 3 hours, and the whole is kept over-night. The ethereal solution is then filtered, and the aluminium hydroxide sludge washed with ether. The ethereal solution is dried with calcium chloride, and the ether evaporated. The crude reduction product (about 200 g.), which has an odour which can best be described as that of a mixture of camphor and peppermint, is fractionated as rapidly as possible, since prolonged heating tends to cause the partial elimination of water from the primary reduction product. Further, it is advisable to carry out the fractionation as soon as possible after the completion of the reduction, as standing in contact with even a small quantity of dry ether produces a considerable quantity of high-boiling material, which was not investigated. The bulk of the liquid distils at 119—126°/20 mm., and a small quantity at 138—140°/20 mm. The main fraction, on long standing and strong cooling, deposits a crystalline solid soluble in most organic solvents. Law (J., 1912, **101**, 1016) was unable to find a medium for recrystallisation and records the m. p. of the crude solid as 53—55°. It can, however, be readily crystallised from a mixture of light petroleum (b. p. 40—60°) and ether and has, after one recrystallisation, m. p. 45°, which remains constant even after five recrystallisations. The solid, if not quickly recrystallised, passes into the liquid form on exposure to the atmosphere for several days (Found for solid, m. p. 45° : C, 72·7; H, 11·0. Found for the liquid, b. p. 122—124°/20 mm.: C, 72·6; H, 11·2. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·0%).

The *semicarbazone* of the solid form is formed after some standing and crystallises from alcohol in hard prisms, m. p. 185° (Found :

C, 60·0; H, 9·3; N, 18·7. $C_{13}H_{25}O_2N_3$ requires C, 59·8; H, 9·6; N, 18·4%). No disemicarbazone could be detected.

The *semicarbazone* of the liquid form, prepared in the usual manner, after several recrystallisations from methyl alcohol, melts constantly at 165° (Found: N, 18·6%). No trace of a disemicarbazone could be detected.

The *benzoyl* derivative of the solid form is prepared by dissolving 1 g. of the solid in 4 g. of pure pyridine and slowly adding 1·5 g. of freshly-distilled benzoyl chloride. The colour of the solution gradually darkens and after ½ hour the whole is poured into excess of dilute hydrochloric acid (1 : 1). The yellowish-brown oil produced is isolated by means of ether (the ethereal solution being washed with dilute sodium bicarbonate solution and with water and dried with sodium sulphate) and solidifies after being kept in a vacuum desiccator for 2 months. It crystallises from methyl alcohol in lustrous plates, m. p. 115° (Found: C, 75·3; H, 8·5. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

The *benzoyl* derivative of the liquid form is prepared in a similar manner, except that the benzoyl chloride is added to the pyridine solution cooled to − 5° and the whole is kept for 2 days. The yellowish-brown oil thus obtained solidifies when a small quantity of the oil is removed by distillation in a vacuum. The monobenzoyl derivative separates from a mixture of light petroleum (b. p. 40—60°) and sodium-dried ether in thick needles, m. p. 42° (Found: C, 75·4; H, 8·4. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

Oxidation with Sodium Hypobromite.—The procedure of Baeyer (*Ber.*, 1896, **29**, 25) is followed for the oxidation of the liquid fraction, b. p. 120—125°/20 mm. A quantitative yield of bromoform corresponding to one acetyl group is obtained, but the only oxidation product which can be isolated consists of a small quantity of viscid gum. A portion crystallises after several months and melts at 122—123°. The acid yields sparingly soluble silver and barium salts, but sufficient could not be isolated to admit of its full characterisation.

Oxidation with Nitric Acid.—The only product which can be isolated by the oxidation of the liquid, b. p. 120—125°/20 mm., by concentrated nitric acid is oxalic acid.

Oxidation with Potassium Permanganate.—The substance is scarcely affected by permanganate.

Oxidation with Chromic Acid.—10 G. of the liquid, b. p. 120—126°/20 mm., are dissolved in 160 c.c. of glacial acetic acid, and a solution of 100 g. of chromic acid in 160 c.c. of 50% acetic acid is added. After the initial vigorous reaction has subsided, the mixture is refluxed for 1 hour. The product is distilled in steam until the distillate is no longer acid; the distillate is extracted six times with ether, and the ethereal extract dried with anhydrous sodium sulphate. The residue, after removal of the ether, consists of a solution of the oxidation product in acetic acid. The latter is almost completely removed by distillation in a vacuum; a crystalline acid, m. p. 198° (rapid heating), is then obtained. Its identity with tetramethylsuccinic acid was established by analysis (Found: C, 55·1; H, 8·0. Calc.: C, 55·2; H, 8·0%) and by conversion into the anil.

The anil of tetramethylsuccinic acid is obtained by heating 0·4 g. of the acid (m. p. 198°) with 0·4 g. (2 mols.) of freshly distilled aniline to the boiling point for a few moments; the whole solidifies on cooling in ice. The excess of aniline is removed by washing with dilute hydrochloric acid. The anil (0·5 g.) separates from dilute alcohol in colourless needles, m. p. 87—88° (compare Auwers and Gardner, *Ber.*, 1890, **23**, 3622; Auwers, *Annalen*, 1896, **292**, 176, who give m. p. 88°) (Found: N, 6·2. Calc.: N, 6·1%).

Identical results are obtained on oxidation of the solid form of the reduction product with chromic acid under similar conditions.

In conclusion, I wish to express my indebtedness to the Chemical Society for a grant which has partly defrayed the expenses incurred in the research, and to Prof. J. F. Thorpe, F.R.S., and Dr. E. H. Farmer for their kind interest in this investigation.

Imperial College of Science and Technology,
South Kensington. [*Received, January* 10*th*, 1927.]

XCI.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Ring Systems. Part I. The Substituted Glutarimides.*

By Sarbbani Sahay Guha Sircar.

The modified strain theory developed by Thorpe and Ingold to explain the relative stabilities of various ring systems has on the whole received ample general experimental confirmation by the work of these and other workers. Their investigations, however, with few exceptions, involved experimental conditions of such a drastic nature that the quantitative comparison of the stabilities of the various systems was a matter of considerable difficulty, and frequently corrections had to be applied for one or more side-reactions which were difficult to control. Though these phenomena were successfully unravelled by these chemists, the difficulty in the way of the ideal solution of the problem could not fail to be noticed. This difficulty was partly solved by Ingold, Sako, and Thorpe (J., 1922, **121**, 1177) by studying the hydrolysis under mild conditions of a number of substituted hydantoins; but the necessary variety of substituted hydantoins is not easy to obtain. Moreover, although the work on hydantoins brought forward strong evidence in support of the modified strain theory, it seemed remarkable that the influence of the substituents was completely unaffected by the presence of two nitrogen atoms in the ring, the valency direction of each of which could not fail to be affected in the same way by the substituents. In other words, the disturbing factors introduced by the nitrogen atoms and the carbonyl groups made the problem more complicated than was desirable.

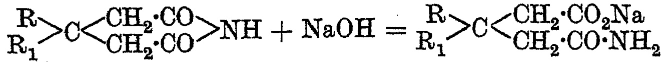
It was considered that heterocyclic rings, such as imides, anhydrides, and lactones, which are opened under mild conditions without complicated side-reactions, would be more suitable for a quantitative study of ring stability. Although a considerable amount of work has been done on the stability of anhydrides by Voermann, Rivett and Sidgwick, Böeseken and his collaborators, and by Verkade and Hjelt, it affords no substantial contribution towards a solution of the present problem.

Sporadic studies of the hydrolysis of a few imides by Miolati (*Atti R. Accad. Lincei*, 1894, **3**, i, 515; 1896, **5**, ii, 375) and of a few lactones by Hjelt (*Ber.*, 1891, **24**, 1236) and by Henry (*Z. physikal. Chem.*, 1892, **10**, 96) throw but little light on the subject under discussion.

The method employed by Miolati and by Henry has now been utilised to work out the comparative rates of hydrolysis of the ring systems mentioned above. It is hoped that by studying the various combinations of the carbon atoms, the carbonyl group, and the hetero-atom, some information may be obtained on the actual effect of the substituting hydrocarbon radicals unaffected by other factors.

The evidence thus obtained from the hydrolysis experiments points unmistakably to the well-marked influence of the substituents in modifying the stability of the various systems in the direction indicated by the modified strain theory. The fact that the ring opens at the hetero-atom, and not at any of the carbon atoms of the ring, probably diminishes the effective manifestation of the molecular strain contributed, if at all, by the distortion of the bonds of the nitrogen or the oxygen atom, unless we assume that the bonds of atoms with "residual valency" may be of a more pliant and accommodating nature than carbon bonds are known to be. This discussion will be amplified, however, in a future communication.

The present paper is concerned with a study of the velocity of hydrolysis of a number of substituted glutarimides, the various substituents being H,H; Me,H; Et,H; Me,Me; Me,Et; Et,Et; *cyclo*pentane, and *cyclo*hexane. In the presence of dilute caustic soda, the reaction



$$\frac{R}{R_1}>C<\frac{CH_2\cdot CO}{CH_2\cdot CO}>NH + NaOH = \frac{R}{R_1}>C<\frac{CH_2\cdot CO_2Na}{CH_2\cdot CO\cdot NH_2}$$

was found to be bimolecular, having a suitable velocity at 25°. Complications due to side reactions took place if the reaction was prolonged beyond the early stages. Another disturbing factor is the presence in the imide of traces of the free acid, which in the form of its salt has a great catalytic influence on the hydrolysis, the velocity being increased at a rate out of all proportion to the amount of the impurity. This factor was responsible for a number of anomalous results in the preliminary experiments, but was eliminated by more thorough purification of the imides.

The following table shows how closely the experimental data agree with the expectations of the modified strain theory, and also indirectly justifies the method here adopted. The full significance of the actual coefficients is not easy to explain. In the table, 2θ represents the calculated angle between two of the carbon bonds and k represents the velocity coefficients of the reactions.

Substituents.	2θ.	$10k$.	Substituents.	2θ.	$10k$.
H,H	115·3°	0·247	Me,Et	?	0·0124
Me,H	112·5	0·0725	Et,Et	?	0·00435
Et,H	?	0·158	*cyclo*Pentane	107·2°	0·00275
Me,Me	109·5	0·0127	*cyclo*Hexane	105·2	0·00215

EXPERIMENTAL.

Preparation of the Imides.—All the imides were prepared by distilling the dry ammonium salt of the appropriate acid from a small retort under ordinary pressure. A large, smoky flame was used and superheating was avoided, the imides being thus obtained in good yield. They were purified by crystallisation from acetone–ether, and then from hot water, being undecomposed by such treatment. Most of the imides are known, but the di-substituted ones had not previously been prepared by the above method. The m. p.'s of the already-known imides agreed completely with those recorded in the literature. As all the glutaric acids are known, details of their preparation are omitted.

Hydrolysis.—95 C.c. of a $N/190$-solution of the imide (actual weights shown at the head of each table) were placed in a 300 c.c. flask and kept in a thermostat at 25° (± 0·2°). When the solution had attained the temperature of the thermostat, 5 c.c. of $N/10$-sodium hydroxide solution were introduced by means of a pipette and the mixture was well stirred. After 1 minute, portions of 10 c.c. were removed at intervals of 5—10 minutes (depending on the velocity of the reaction), run into about 15 c.c. of ice-cold distilled water, and the unused alkali was titrated with *N*/100- or *N*/200-sulphuric acid. The velocity coefficient was calculated from the formula for a bimolecular reaction $k = x/ta(a - x)$, where t is the time (in minutes), a the initial concentration of imide (corresponding to 10 c.c. of *N*/200-, or 5 c.c. of *N*/100-acid), and x the alkali utilised. No great accuracy is claimed where the velocity is high, but the number of such cases is small. The results of the experiments are given in the Tables I—VIII, the figures in the second column representing c.c. of *N*/100-(or *N*/200-)acid used in the titration.

Glutarimide (see Table I).—Yield, 65·4%. It was crystallised first from acetone and then from water; glistening scales, m. p. 152° (Found: N, 12·1. Calc.: N, 12·4%).

TABLE I.

0·1486 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·2	—
5	2·2	0·0254
10	1·5	0·0233
15	1·05	0·0256
20	0·95	0·0244
27	0·65	0·0248
33	0·55	0·0243
	Mean	0·0247

(Miolati obtained 0·0251.)

TABLE II.

0·1672 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·6	—
5	3·5	(0·0086)
10	2·95	0·0070
15	2·4	0·0072
20	2·05	0·0072
25	1·75	0·0074
30	1·5	0·0074
	Mean	0·00725

β-*Methylglutarimide* (see Table II).—Yield, 68%; crystallised from ether–acetone in scales, m. p. 142—143° (Found: N, 11·3. Calc.: N, 11·0%).

β-*Ethylglutarimide* (see Table III).—Yield, 57%; crystallised from acetone–ether and then from water; scales, m. p. 87° (Found: N, 10·3. Calc.: N, 9·9%).

TABLE III.

0·0742 g. dissolved in 100 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	3·2	—
5	2·4	(0·0216)
10	1·8	0·0177
15	1·425	0·0167
20	1·25	0·0166
25	1·05	0·0150
30	0·90	0·0133
35	0·825	0·0192
	Mean	0·0158

TABLE IV.

0·1854 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·85	—
5	4·05	—
10	4·40	0·00136
15	4·15	0·00136
20	3·95	0·00133
25	3·75	0·00133
30	3·7	0·00117
43	3·45	0·00104
	Mean	0·00127

ββ-*Dimethylglutarimide* (see Table IV).—Yield, 75%; crystallised from water in long needles, m. p. 147° (Found: N, 10·3. $C_7H_{11}O_2N$ requires N, 9·9%).

ββ-*Methylethylglutarimide* (see Table V).—Yield, 70%; crystallised from water in leafy plates, m. p. 127° (Found: N, 9·3. $C_8H_{13}O_2N$ requires N, 9·0%).

TABLE V.

0·0816 g. dissolved in 100 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·8	—
5	4·7	0·00127
10	4·4	0·00136
15	4·2	0·00127
20	3·95	0·00132
25	3·8	0·00126
30	3·7	0·00117
35	3·65	0·00105
	Mean	0·00124

TABLE VI.

0·0846 g. dissolved in 95 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·95	—
5	4·85	(0·000618)
10	4·8	0·000416
20	4·6	0·000434
30	4·45	0·000412
40	4·2	0·000476
50	4·1	0·000439
	Mean	0·000435

ββ-*Diethylglutarimide* (see Table VI).—Yield, 48%; crystallised in glistening plates from water; m. p. 146—147° (Found: N, 8·0. $C_9H_{15}O_2N$ requires N, 8·2%). Owing to its sparing solubility, 0·0846 g. (corresponding to 95 c.c. of *N*/190-solution) of the finely powdered imide was suspended in 95 c.c. of distilled water and kept at 25°; 5 c.c. of *N*/10-sodium hydroxide solution were added, and the imide then dissolved in 5 minutes.

cyclo*Pentanediacetimide* (see Table VII).—Yield, 68%; crystallised in plates from acetone or water, m. p. 153—154° (Found: N, 8·2. $C_9H_{13}O_2N$ requires N, 8·4%).

TABLE VII.

0·2198 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	5·1	—
5	4·90	—
10	4·85	0·000309
20	4·75	0·000263
30	4·65	0·000252
40	4·55	0·000297
50	4·425	0·000261
60	4·3	0·000271
	Mean	0·000275

TABLE VIII.

0·1814 g. dissolved in 95 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	5·0	—
5	4·85	—
10	4·85	0·000309
20	4·8	0·000209
30	4·7	0·000212
40	4·6	0·000217
50	4·5	0·000220
60	4·425	0·000216
	Mean	0·000215

cyclo*Hexanediacetimide* (see Table VIII).—Yield, 70%; crystallised from water in glistening scales, m. p. 169° (Found: N, 7·5. $C_{10}H_{15}O_2N$ requires N, 7·7%).

Summary.

The velocity coefficients for the hydrolysis of a number of substituted glutarimides have been studied with the view of finding how far the order of stability in this series of compounds agreed with the expectations of Thorpe and Ingold's modified strain theory. The agreement is quite satisfactory. The unusual instability of glutarimide itself is very marked, and the effect of the methyl group in increasing the stability is also remarkable. After that, however, there is a steady increase of stability as the series is ascended (H,H; Me,H; Et,H; Me,Me; Me,Et; Et,Et; *cyclo*pentane; *cyclo*hexane).

The author wishes to express his grateful thanks to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in the work, and to the Chemical Society for a Research Fund grant that defrayed a part of the expense.

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[*Received, January 26th,* 1927.]

XCII.—*The Platini-Platino-chloride Electrode. A New Type of Chlorine Electrode.*

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AN inert electrode in a solution of sodium chloroplatinate and sodium chloroplatinite acquires a definite potential. The mechanism of the electrode differs from that of the usual oxidation-reduction type in that there is no change in valency. Measured against a calomel electrode, the platinum of the platini-platino electrode is positive to the mercury. The cell reaction is expressed by

$$2\mathrm{Hg} + \mathrm{Na_2PtCl_6} \longrightarrow 2\mathrm{HgCl} + \mathrm{Na_2PtCl_4} \quad . \quad . \quad (1)$$

the current passing from left to right inside the cell:

$$\overset{-}{\mathrm{Hg}} \mid \mathrm{Hg_2Cl_2,NaCl} \mid \mathrm{NaCl} + \mathrm{Na_2PtCl_6} + \mathrm{Na_2PtCl_4} \mid \overset{+}{\mathrm{Pt}}.$$

The electrode reaction is

$$\bar{\mathrm{P}}\mathrm{t}\bar{\mathrm{C}}\mathrm{l}_6 + 2e \longrightarrow \bar{\mathrm{P}}\mathrm{t}\bar{\mathrm{C}}\mathrm{l}_4 + 2\bar{\mathrm{C}}\mathrm{l}$$

and the *E.M.F.* is given by

$$E = E_0 + RT/2F \,.\, \log\,[\bar{\mathrm{P}}\mathrm{t}\bar{\mathrm{C}}\mathrm{l}_6]/[\bar{\mathrm{P}}\mathrm{t}\bar{\mathrm{C}}\mathrm{l}_4][\bar{\mathrm{C}}\mathrm{l}]^2,$$

or, more exactly, by

$$E = E_0 + RT/2F \,.\, \log a_i/a_o a^2{}_{\mathrm{Cl}} \quad . \quad . \quad . \quad . \quad (2)$$

where a_i, a_o, and a_{Cl} are the activities of the chloroplatinate, the chloroplatinite, and the sodium chloride, respectively.

To test the above relationship, two series of measurements were carried out. In the first, the chloride concentration was kept constant and the $i : o$ ratio varied. In the second, this ratio was constant and the chloride concentration varied. (Here, i and o represent the total concentrations of chloroplatinate and chloroplatinite, respectively.)

The values of E_0 calculated according to the above expression for the two series of measurements are given in Table I (full data in Tables II and III). Since the concentration of sodium chloride is much higher than those of the platinum salts, the ratio of the activities of the latter was assumed to be equal to the ratio of their concentrations, *i.e.*, $a_i/a_o = i/o$. The activity of the chlorine ion was taken to be the same as in the corresponding sodium chloride solution.

TABLE I.

Series I.			Series II.		
$i : o$ ratio.	NaCl (mols./litre).	E_0 (volts).	$i : o$ ratio.	NaCl (mols./litre).	E_0 (volts).
0·5804	1	0·7191	1·4642	1·0000	0·7202
0·9199	,,	0·7217	,,	0·7000	0·7184
1·4642	,,	0·7202	,,	0·5000	0·7176
2·0441	,,	0·7211	,,	0·2000	0·7173
2·9282	,,	0·7206	,,	0·1000	0·7165
5·3773	,,	0·7210	,,	0·0500	0·7143
11·8033	,,	0·7213	,,	0·0100	0·7060
29·5633	,,	0·7211	,,	0·0048	0·6985

It will be seen that with constant sodium chloride concentration a satisfactorily constant value for E_0 is obtained. The value, however, changes slightly with change in the sodium chloride environment. This suggests that the ratio of the activities of the chloro-platinate and -platinite ions is not independent of the surroundings and that this ratio should be expressed as a function of the sodium chloride concentration, *i.e.*, $a_i/a_o = K \, . \, i/o$, where K is a function of the ionic strength of the sodium chloride * solution. When K is constant, this leads to the expression

$$E = (E_0 + RT/2F \, . \log K) + RT/2F \, . \log (i/o) - RT/F \, . \log a_{Cl} \quad . \quad . \quad . \quad . \quad (3)$$

the given values of E_0 in Series I being really values of

$$(E_0 + RT/2F \, . \log K),$$

where K corresponds to M-sodium chloride solution.

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* At low concentrations of sodium chloride it would possibly be preferable to use the total ionic strength of the solution instead of that of the sodium chloride alone.

If the values of E in Series II are plotted against a_{Cl}, a straight line is obtained for the first six values. A straight line would result if $\log K$ were itself a linear function of $\log a_{Cl}$, *i.e.*, if $\log K = \alpha + \beta \log a_{Cl}$, where α and β are constants.

Making this assumption, we have

$$E = E_0 + RT/2F \,.\, (\beta - 2) \log a_{Cl} + RT/2F \,.\, \log i/o + RT/2F \,.\, \log \alpha$$

$$\text{or } E = (E_0 + C) + RT/2F \,.\, (\beta - 2) \log a_{Cl} + RT/2F \,.\, \log i/o \quad (4)$$

where C is an undetermined constant which cannot be evaluated until the nature of K is known. As will be seen later, this expression gives a satisfactorily constant value for $(E_0 + C)$.

EXPERIMENTAL.

The sodium chloroplatinate was obtained by dissolving platinic chloride in sodium chloride and crystallising the hexahydrate. The chloroplatinite was made by converting platinum tetrachloride into dichloride by heating at 350° and dissolving the residue in hydrochloric acid. This solution was neutralised with barium carbonate, and on evaporation gave dark red crystals of $BaPtCl_4,3H_2O$, contaminated with a little barium chloride. Treatment of this salt with sodium sulphate gave the corresponding sodium salt; owing to its high solubility it was impossible to purify it by crystallisation (Found: H_2O, 12·11; NaCl, 8·01; Na_2PtCl_4, 79·88%). Since, however, sodium chloride was used as the electrolyte, the removal of the small amount present as impurity was unnecessary. In making up the solutions the sodium chloroplatinite was weighed anhydrous. Except for solutions 6, 7, and 8 of the first series and for the more concentrated platinum solutions, the electrode mixtures were made by adding 3—10 c.c. of a stock solution to the required amount of sodium chloride and then diluting to 25 c.c. Solutions 6, 7, and 8 were made by taking weighed amounts of the two salts.

The Cell.—The electrode vessels were of the type commonly used for single electrodes, with a tap sealed in the connecting tube to prevent diffusion. The electrode was measured against a normal calomel electrode containing sodium chloride instead of potassium chloride. Platinised glass was found to be the most suitable form of electrode, equilibrium being established after about 24 hours. The cells were measured at 25°, an air thermostat being used to control the temperature. The measuring apparatus consisted of a Pye potentiometer, a Cambridge Instrument Company moving-coil galvanometer, and a Cambridge standard cadmium cell.

Results.

After attainment of equilibrium, readings varied by less than 0·1 millivolt over a period of several hours, except in the case of the 0·2N-sodium chloride solution, where the variation from the mean over 6 hours was 0·6 millivolt. The values were tested for reproducibility. For solution 8 of the first series, the first sample gave a mean value of 0·5057, with no variation in the readings in 8 hours after attainment of equilibrium; the second sample gave a mean value of 0·5057, the readings varying from 0·5056 to 0·5058.

The effect of change in the values of i and o with a constant ratio between them was as follows, the sodium chloride concentration being N.

i (mol./litre).	o (mol./litre).	$i : o$.	*E.M.F.* of cell.
(*a*) 0·005548	0·009559	0·580	0·4549
(*b*) 0·0005548	0·0009559	0·580	0·4532

A solution with concentrations one-tenth of those in (*b*) did not give constant readings.

Table II gives the results of the first series of readings in N-sodium chloride solution. The value used for the calomel electrode potential was 0·2731 volt. Table III gives the results of the second series of measurements, in which a liquid potential was introduced between the connecting liquid and the electrode solution, diminishing the *E.M.F.* measured. This potential was calculated from the relationship

$$E_L F = (n_k - n_a) RT \log C_1\alpha_1/C_2\alpha_2$$

where E_L is the liquid potential, n_k and n_a are the transport numbers of the kation and anion, respectively, and α_1 and α_2 are the activity coefficients of the sodium chloride solutions.

The calculation of β in equation (4) was carried out by taking the values of E found in experiments 2 and 6 (Table III), whence, by subtraction,

$$(E_2 - E_6) = RT/2F \,.\, (\beta - 2)[\log (a_{\text{Cl}})_6 - \log (a_{\text{Cl}})_2]$$

and hence $\beta = 0{\cdot}1317$.

The Effect of Temperature on the E.M.F. *of the Electrode.*

The potentials of solutions 6 and 7 of the first series were measured at 21°, 25°, and 30°, with the following results :

$i : o$.	*E.M.F.* (volt) of electrode.		
	21°	25°	30°
(6) 5·3773	0·7532	0·7537	0·7537
(7) 11·8033	0·7627	0·7641	0·7642

TABLE II.

Cell $\overset{-}{\text{Hg}} \mid \text{Hg}_2\text{Cl}_2$, N-NaCl $\mid$ N-NaCl + Na_2PtCl_6 + $\text{Na}_2\text{PtCl}_4 \mid \overset{+}{\text{Pt}}$. Temperature 25°.

($a_{\text{Cl}} = 0{\cdot}650$.)

No.	$i \times 10^3$ (mols./litre).	$o \times 10^3$ (mols./litre).	$\frac{i}{o}$.	*E.M.F.* cell.	*E.M.F.* electrode, *E*.	$\frac{RT}{2F}(\beta-2)\log a_{\text{Cl}}$.	$\frac{RT}{2F}\log\frac{i}{o}$.	$E_0 + C$.
1	0·5548	0·9559	0·5804	0·4532	0·7232	0·01035	−0·0070	0·7199
2	0·9187	0·9987	0·9199	0·4617	0·7317	0·01035	−0·0011	0·7225
3	1·4623	0·9987	1·4642	0·4662	0·7362	0·01035	0·0049	0·7209
4	2·041	0·9987	2·0441	0·4714	0·7414	0·01035	0·0092	0·7218
5	2·9243	0·9986	2·9282	0·4751	0·7455	0·01035	0·0138	0·7213
6	5·3703	0·9987	5·3773	0·4837	0·7537	0·01035	0·02163	0·7218
7	11·789	0·9987	11·8033	0·4941	0·7641	0·01035	0·0317	0·7220
8	29·524	0·9987	29·5633	0·5057	0·7757	0·01035	0·0436	0·7218
							Mean	0·7215

TABLE III.

$i : o$ = constant = 1·4642. Temperature 25°.

Cell $\overset{-}{\text{Hg}} \mid \text{Hg}_2\text{Cl}_2$, N-NaCl $\mid$ xNaCl + 0·001462 Na_2PtCl_6 + 0·0009987 $\text{Na}_2\text{PtCl}_4 \mid \overset{+}{\text{Pt}}$.

NaCl (mols./litre).	α_{NaCl}.	a_{NaCl}.	*E.M.F.* cell.	*E.M.F.* electrode, E_1.	Liquid potential, E_2.	$E_1 + E_2$. (*E*).	$\frac{RT}{2F}(\beta-2)\log a_{\text{Cl}}$.	$\frac{RT}{2F}\log\frac{i}{o}$.	$E_0 + C$.
1·0000	0·650	0·650	0·46615	0·7362	0·0000	0·7362	0·01035	0·0049	0·7209
0·7000	0·673	0·471	0·47099	0·7410	0·0016	0·7426	0·0181	0·0049	0·7196
0·5000	0·689	0·344	0·47665	0·7467	0·0032	0·7499	0·0256	0·0049	0·7194
0·2000	0·752	0·150	0·49353	0·7635	0·0073	0·7707	0·0455	0·0049	0·7203
0·1000	0·798	0·0798	0·50580	0·7758	0·0105	0·7863	0·0602	0·0049	0·7213
0·0500	0·842	0·0421	0·51694	0·7869	0·0137	0·8006	0·0761	0·0049	0·7196
0·0100	0·922	0·00922	0·5400	0·8100	0·0213	0·8313	0·1126	0·0049	[0·7138]
0·00479	0·940	0·00450	0·5473	0·8173	0·0250	0·8423	0·1298	0·0049	[0·7076]
								Mean	0·7202

*In the first series $dE/dT = 0{\cdot}000033$; in the second $dE/dT = 0{\cdot}000084$. At 25° the *E.M.F.* of the cell is 0·4837 and 0·4941 in the two series. Applying the Gibbs–Helmholtz equation, $nFE - Q = nFTdE/dT$ (where Q is the heat evolved in the cell-reaction at constant temperature and pressure), to these data we obtain

$$Q = 21{,}830 \text{ cals. from 1st series}$$
$$21{,}610 \quad ,, \quad ,, \text{ 2nd} \quad ,,$$

The heat of formation of 2HgCl = 62,600 cals. and thus the heat of formation of Na_2PtCl_6 from Na_2PtCl_4 and Cl_2 is seen from the equation (1) for the cell-reaction to be 40,770 cals. (1st series), 40,990 cals. (2nd series). We may compare this value with that of Thomsen from direct heat measurement, *viz.*, 42,000 cals.

Summary.

The potential of the platini-platino-chloride electrode has been measured. The *E.M.F.* varies according to the equation

$$E = (E_0 + C) + RT/2F \,.\, (\beta - 2) \log a_{Cl} + RT/2F \,.\, \log i/o$$

where β and C are constants.

The temperature coefficient of the cell was determined. From the Gibbs–Helmholtz equation the heat of formation of sodium chloroplatinate from the chloroplatinite and chlorine was calculated as 40,880 cals.

Our best thanks are due to Professor Donnan for his advice and help.

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XCIII.—*The Viscosity of Ether at Low Temperatures.*

By EBEN HENRY ARCHIBALD and WILLIAM URE.

As explained in a former paper (J., 1924, **125**, 726), we wished to know the rate of change of viscosity with temperature of certain organic liquids at low temperatures. The viscosity of acetone has been investigated (*loc. cit.*). The present experiments deal with the viscosity of ethyl ether over a temperature range of 0° to − 110°, the measurements being made at 10° intervals.

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* These are the values of dE/dT at 25° determined graphically from the *E.M.F.*–temperature curve.

Materials and Apparatus.—"Anhydrous ether distilled over sodium" was treated with three successive portions of water to remove alcohol, dried over calcium chloride, then over sodium and distilled.

The Ostwald type of viscometer was used and the apparatus was set up as shown in Fig. 1. To prevent atmospheric moisture from condensing in the viscometer both ends were connected to calcium chloride drying tubes. Careful observation convinced us that no difference in the time of flow was caused by inserting these tubes. The required volume of ether was transferred from a supply flask by means of a syphon, one end of which passed into the larger end of the viscometer. The liquid was drawn up to the graduation above the bulb by means of an aspirator.

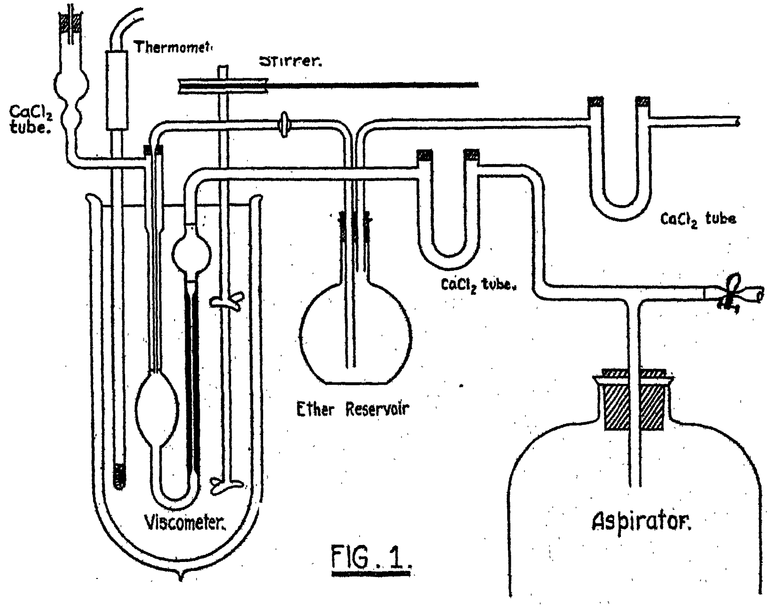


FIG. 1.

The cryostat consisted of a large unsilvered Dewar tube of about 10 cm. internal diameter which was almost filled with dry ether. For measurements from 0° to − 75° carbon dioxide snow was used to regulate the temperature, small amounts being added at intervals. Below − 75°, liquid air was used, and was handled after the manner devised by Henning (*Z. Instrument.*, 1913, **33**, 33).

The temperatures were indicated by a platinum resistance thermometer of the bridge type, Leeds and Northrop Meter Bridge, No. 4201, being used, reading to 0·0001 ohm, corresponding to about 0·01°. The resistance element was contained in a quartz tube which also contained gold compensating leads. The galvanometer was observed with lamp and scale. The resistance of the leads was eliminated by taking the mean of two readings at opposite positions of the commutator switch.

The thermometer was standardised by the Bureau of Standards in September 1923, and δ in the Callendar equation was found to be 1·50. On installation in this laboratory, the thermometer was checked at 0°, and observations were made at the temperatures of the ether and solid carbon dioxide mixture (— 78·34° at atmospheric pressure) and of boiling oxygen (— 182·95°) to determine the deviation from the parabolic formula. At — 78·34°, the thermometer read 0·04° low and at — 182·95°, 1·77° low. These values correspond to Henning's corrections to the parabolic formula (*Ann. Physik*, 1913, **40**, 735), and these corrections were accordingly used. A resistance-temperature chart was plotted and used to obtain the temperatures at which the viscosity measurements were made.

At the higher temperatures, the cryostat could be controlled within 0·1°, and below — 30° within 0·2°.

For measurements between 0° and — 30°, a viscometer having a very fine capillary was used. The water rate at + 20° was 385·2 sec., and the maximum time of flow of ether was 211·2 sec. at — 32·1°. At the lower temperatures, a tube of somewhat larger bore was employed. The water rate in this case was 207·6 sec. at 0° and the maximum time of flow for the ether 341·2 sec. at — 109·8°.

By means of a stop watch, the time of flow could be measured to within 0·2 sec.

Results.—The viscosities were calculated from the observed times of flow in the same manner as in the previous paper (*loc. cit.*) using the equation

$$\eta = \frac{dt}{d_w t_w}\left(\eta_w + \frac{m d_w V}{8\pi l t_w}\right)\{1 - 0{\cdot}000008(0 - t)\} - \frac{m d V}{8\pi l t},$$

where η is the coefficient of viscosity of the liquid, V the volume of liquid which flows through the capillary in the time t, d the density of the liquid, l the length of capillary, and m a constant = 1·12 (Boussinesq, *Compt. rend.*, 1891, **112**, 1099); those symbols with subscript w relate to water.

This expression includes corrections for kinetic energy and for the change in the dimensions of the instrument with temperature. The density values were taken from the work of Taylor and Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 2456).

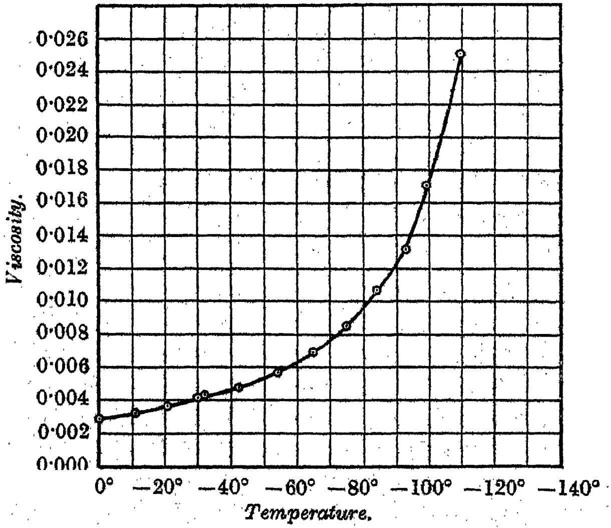
The results are given in Table I, in which the viscosities are expressed in absolute units, that of water at 0° being taken as 0·01792. In most cases, they are given to four significant figures, which is the accuracy warranted by the time measurement and temperature control. Where the time of flow was relatively short or the agreement in a series of measurements not close, the results are given to only three significant figures. For completeness, the densities at the various temperatures are included in the table.

TABLE I.

Temp.	*d.*	η.	Temp.	*d.*	η.
0·0°	0·73629	0·002903	− 64·5°	0·80554	0·00693
−10·2	0·74750	0·003239	− 75·4	0·81695	0·008664
−20·2	0·75842	0·003636	− 84·4	0·82621	0·010747
−30·1	0·76906	0·004109	− 92·2	0·83426	0·01334
−32·1	0·77121	0·00420	− 99·8	0·84180	0·01708
−43·0	0·78289	0·00485	−109·8	0·85210	0·02514
−53·9	0·79443	0·00574			

Fig. 2 shows a plot of viscosity against temperature. As in the case of acetone, the curve rises very steeply at the lower temperatures.

FIG. 2.



To illustrate further this rapid rate of increase of viscosity, some values of the temperature coefficient have been calculated at each end of the temperature range. These are expressed in Table II as percentage values of the viscosity value at the end of each 10°-interval, *i.e.*, $\alpha = 100(\eta_2 - \eta_1)/\eta_2(T_1 - T_2)$.

TABLE II.

Temperature Coefficients of Viscosity of Ether.

η_1 = viscosity at temp. T_1; η_2 = viscosity at temp. T_2.

T_1.	T_2.	a.	T_1.	T_2.	a.	T_1.	T_2.	a.
0°	−10°	0·99	−40°	−50°	1·33	− 80°	− 90°	2·26
−10	−20	1·10	−50	−60	1·49	− 90	−100	2·72
−20	−30	1·17	−60	−70	1·86	−100	−110	3·24
−30	−40	1·24	−70	−80	1·89			

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[*Received, December 23rd*, 1926.]

XCIV.—*Electrometric Study of the Precipitation of Phosphates.*

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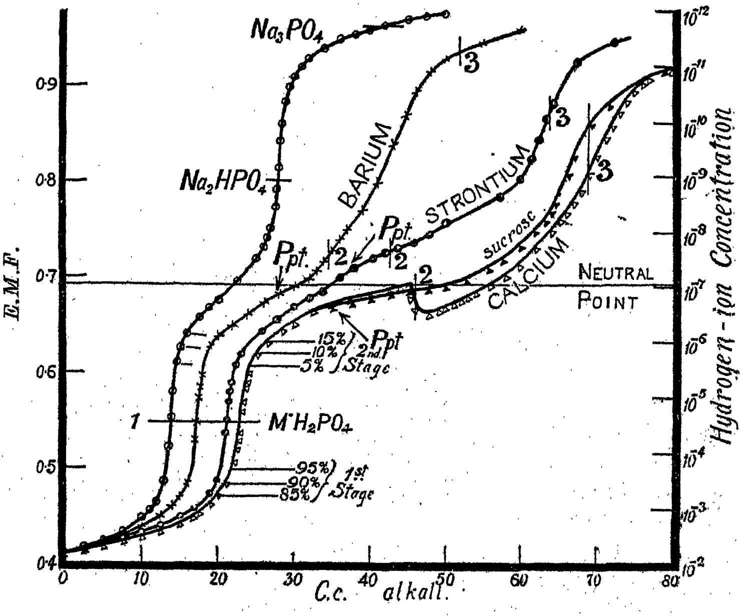
AN attempt is made in this paper to correlate the dissociation of phosphoric acid with the precipitation reactions in which it is involved. Phosphoric acid behaves in its first stage of ionisation as a strong acid, $K_1 = 9{\cdot}4 \times 10^{-3}$, in its second as a weak acid, $K_2 = 1{\cdot}4 \times 10^{-7}$, and in its third stage as an extremely weak acid, $K_3 = 2{\cdot}7 \times 10^{-12}$, so weak that its dissociation can only just be determined. It appears probable, from the very low order of magnitude of K_3, that the third hydrogen atom of phosphoric acid might be incapable of reacting with the majority of weak bases unless the phosphates happen to be very insoluble and the phosphate-ion concentrations of the mother-liquors are kept sufficiently large to exceed the solubility products without permitting the hydrogen-ion concentrations to become so small as to cause precipitation of the hydroxides. Hence, in order to study the part played by phosphoric acid in the various precipitation reactions, the hydrogen-ion concentrations which prevail throughout their courses have been measured by means of the hydrogen electrode. Two series of potentiometric titrations with the hydrogen and normal calomel electrodes have been made in the manner outlined in previous communications (J., 1924, **125**, 1572; 1925, **127**, 2110): the first comprises the reactions between solutions of phosphoric acid and strong bases, *viz.*, the hydroxides of sodium, calcium, barium, and strontium; and the second series deals with the action of trisodium phosphate, chosen because it involves the third stage of ionisation, on solutions of salts of typical metallic bases. A titration by lime water of phosphoric acid in a solution of sucrose was included in the first series in view of the discordant observations of Wendt and Clarke (*J. Amer. Chem. Soc.*, 1923, **45**, 881) and Hoffman and Gortner

(*J. Physical Chem.*, 1925, **29**, 769). [See also Holt, LaMer, and Chown (*J. Biol. Chem.*, 1925, **64**, 509) and Farnell (*J. Soc. Chem. Ind.*, 1926, **45**, 343T).]

Series I.

Fig. 1 gives the hydrogen-electrode titration curves at 20° of (1) 100 c.c. of 0·01277M-H_3PO_4 with 0·0919N-NaOH, (2) 100 c.c. of 0·00965M-H_3PO_4 with 0·0558N-$Ba(OH)_2$, (3) 100 c.c. of 0·00765M-H_3PO_4 with 0·0359N-$Sr(OH)_2$, (4) 100 c.c. of 0·01024M-H_3PO_4 with 0·0447N-$Ca(OH)_2$, and (5) 100 c.c. of 0·01024M-H_3PO_4 containing 5 g. of sucrose with 0·0447N-$Ca(OH)_2$. With the exception of the sodium hydroxide titration and the alkaline-earth titrations up to the addition of the first equivalent, the *E.M.F.*'s recorded were not true equilibrium values, but were those indicated immediately after each addition of the reactant, for, as Wendt and Clarke observed in their lime-water titrations, the initial *P.D.*'s become smaller when the solutions stand for some time, through the slow reactions which take place between the precipitate and the added alkaline earth.

FIG. 1.



It is necessary to consider the three dissociation constants of phosphoric acid which have been found to satisfy the sodium hydroxide titration curve, especially in view of the different values of K_3 which have been reported. Thus Abbott and Bray (*J. Amer. Chem. Soc.*, 1909, **31**, 729) gave K_3 at 18° as $3{\cdot}6 \times 10^{-13}$, whereas Prideaux and Ward (J., 1924, **125**, 423) have recently shown that their p_{H} measurements and those of other workers give values ranging from $1{\cdot}54$ to $5{\cdot}3 \times 10^{-12}$. Excluding the small portions of the curve about the points of inflexion, the hydrogen-ion concentrations corresponding to the first two sections of the curve are due (see Britton, J., 1925, **127**, 1896) entirely to the equilibria governed by $K_1 = [H^{\cdot}][H_2PO_4']/[H_3PO_4]$ and $K_2 = [H^{\cdot}][HPO_4'']/[H_2PO_4']$, and consequently the simple method adopted in calculating the dissociation constants of malonic acid is applicable. The large hydroxyl-ion concentrations produced during the neutralisation of disodium phosphate with sodium hydroxide are due to a portion of the added alkali taking part in the hydrolysis—in effect remaining unattacked. The concentration of this unattacked alkali may be found directly from the *E.M.F.*'s, assuming the complete ionisation of the solutes, and therefore the concentration of sodium phosphate actually formed is the difference between this and the concentration which would have been produced if all the added alkali had formed trisodium phosphate. The method of calculating K_3 is identical with that previously used to find the dissociation constant of dextrose. Table I gives the *E.M.F.*'s of the hydrogen electrode, compared with the normal calomel electrode, for the titration of phosphoric acid with sodium hydroxide, together with the various calculated ionic concentrations and the dissociation constants to which they lead.

The values of the dissociation constants given in the last column show that the values $K_1 = 9{\cdot}4 \times 10^{-3}$, $K_2 = 1{\cdot}4 \times 10^{-7}$, and $K_3 = 2{\cdot}7 \times 10^{-12}$ reproduce fairly well the three sections of the titration curve. The values of K_1 and K_2 are slightly lower than Abbott and Bray's (*viz.*, $K_1 = 1{\cdot}1 \times 10^{-2}$, $K_2 = 1{\cdot}95 \times 10^{-7}$), whereas that of K_3 is seven times greater than their value. It is, however, in agreement with the recent value of Prideaux.

On comparing the alkaline-earth titration curves, up to the points corresponding to the beginning of precipitation, with that of sodium hydroxide, it will be seen that they cover almost identical ranges of hydrogen-ion concentration. In the lime-water titration precipitation was delayed until 1·53 equivs. (= 35 c.c.) had been added and p_{H} 6·72 was attained. On standing over-night, a solution of the same concentrations deposited an appreciable amount of precipitate and its p_{H} fell to 5·98; in fact, precipitates were formed when solutions were allowed to stand which contained only just over 1 equiv. of calcium hydroxide. The delay in precipitation and the high initial p_{H} were caused by neutralisation taking place

TABLE I.

Titration of 100 c.c. of 0·01277M-H_3PO_4 with 0·0919N-NaOH at 20°.

(NaH_2PO_4 = 13·9 c.c.; Na_2HPO_4 = 27·8 c.c.)

NaOH (c.c.).	*E.M.F.*	p_H.	$[H_2PO_4'] \times 10^3$.	$[H_3PO_4] \times 10^3$.	$K_1 \times 10^3$.
0·0	0·408	2·14	7·24	5·53	9·55
2·55	0·416	2·28	7·54	4·92	8·13
5·0	0·423	2·40	8·36	3·80	8·71
7·5	0·433	2·57	9·10	2·78	8·91
10·0	0·447	2·81	9·90	1·71	9·12
11·0	0·455	2·94	10·26	1·24	9·55
12·0	0·464	3·10	10·64	0·76	11·22
13·0	0·486	3·48	10·90	0·36	10·00
13·5	0·521	4·10	11·00	0·26	3·31
				Mean	9·4

NaOH (c.c.).	*E.M.F.*	p_H.	C.c. NaH_2PO_4.	C.c. Na_2HPO_4.	$K_2 \times 10^7$.
14·5	0·610	5·60	13·3	0·6	1·12
15·0	0·625	5·86	12·8	1·1	1·18
16·0	0·640	6·11	11·8	2·1	1·38
17·5	0·657	6·40	10·3	3·6	1·38
20·0	0·675	6·71	7·8	6·1	1·51
22·5	0·695	7·06	5·3	8·6	1·41
25·0	0·719	7·47	2·8	11·1	1·35
26·0	0·731	7·67	1·8	12·1	1·44
27·0	0·751	8·01	0·8	13·1	1·35
27·5	0·773	8·39	0·3	13·6	1·82
				Mean	1·4

NaOH (c.c.).	*E.M.F.*	p_H.	$[PO_4'''] \times 10^3$.	$[HPO_4''] \times 10^3$.	$K_3 \times 10^{12}$.
29·0	0·883	10·28	0·66	9·24	3·72
30·0	0·909	10·72	1·02	8·80	2·24
31·0	0·921	10·92	1·42	8·33	2·04
32·0	0·928	11·05	1·80	7·87	2·04
34·0	0·940	11·26	2·43	7·10	1·91
36·0	0·949	11·40	3·03	6·36	1·91
38·0	0·954	11·49	3·70	5·55	2·19
40·0	0·959	11·57	4·29	4·83	2·40
42·5	0·964	11·66	4·91	4·05	2·63
45·0	0·968	11·72	5·65	3·16	3·39
47·5	0·973	11·81	5·81	2·85	3·16
50·0	0·975	11·85	6·52	1·99	4·57
				Mean	2·7

immediately, whereas the precipitation from the supersaturated solution was a matter of time. Had neutralisation only taken place, the hydrogen-ion concentration would have been equal to $[H_2PO_4'] \times K_2/[HPO_4''] = (2 - n) \times 1{\cdot}4 \times 10^{-7}/(n - 1)$, where n is the number of equivs. of alkaline earth, from which it follows that the p_H of the calcium solution when on the point of precipitation should have been 6·91, which is slightly higher than the observed value, 6·72, the difference evidently being due to the precipitation reaction having proceeded to a small extent. The presence of sucrose in the phosphoric acid solution did not impede precipitation. In the baryta titration, 1·62 equivs. were required to start precipitation, which took place at p_H 6·88; on standing over-night further precipitation occurred and the p_H of the solution fell to 6·07. Strontium hydroxide solution produced a precipitate with 1·78 equivs. (38 c.c.); the p_H was then 7·34, but it became 6·60 after standing over-night, more precipitate having separated. These titrations up to the point of precipitation consisted chiefly of neutralisation, for by calculation it is found that for neutralisation alone the p_H should have been 7·07 in the barium titration instead of 6·88 observed, and 7·40 in the strontium titration instead of 7·34.

The precipitates first formed were the monohydrogen phosphates, $M^{\cdot\cdot}HPO_4$, which by the addition of more alkaline earth became converted into the normal phosphates, $M_3(PO_4)_2$. The inflexion in the baryta-titration curve occurred during the addition of the third equiv., and therefore the precipitate was a mixture of di- and tribarium phosphates, whereas in the strontia curve the inflexion was not produced until the third equiv. had been added, showing that the precipitate was the normal strontium phosphate. The final inflexion in the calcium hydroxide titration occurred when the third equiv. had been added, suggesting that at that stage the precipitate was tricalcium phosphate. It will, however, be observed that further additions of lime water did not cause as great an increase in p_H as in the other titrations. This was due to the absorption by the calcium phosphate of some calcium hydroxide thus rendering the phosphate basic. Bassett (J., 1917, **111**, 620) found that one molecule of tricalcium phosphate can absorb one-third of a molecule of calcium hydroxide to form "hydroxyapatite," $3Ca_3(PO_4)_2,Ca(OH)_2$; he believes that this is the calcium phosphate which can permanently exist in the soil under ordinary conditions.

The variation in hydrogen-ion concentration, which occurred in the lime-water reaction just after two equivs. had been added, is remarkable in that the addition of more reactant actually caused an increase in the concentration of hydrogen ions. Wendt and Clarke (*loc. cit.*) found a similar change, but theirs occurred while the second equiv. was being added, doubtless owing to longer times being allowed to elapse before making measurements. An examination of the p_H data corresponding to the addition of the second equiv. of calcium hydroxide in the present titration reveals that the high p_H values were such as would be produced by a large concentration of HPO_4'' ions, caused through supersaturation, as compared with that of H_2PO_4' ions. Assuming that in the first place only the dicalcium phosphate was being formed and partly precipitated, it appears that, when the second equiv. of lime water had been added, the concentration of monocalcium phosphate, and therefore of H_2PO_4' ions, had been reduced to a minimum, the little remaining being produced by the hydrolysis of the precipitate. A sudden diminution in the concentration of HPO_4'' ions would lead to a sudden increase in p_H. Actually a sudden decrease in p_H was obtained and this was accompanied by further precipitation. It appears probable therefore that the added calcium hydroxide reacted with the dicalcium phosphate remaining in solution, causing precipitation of the tricalcium salt, and in so doing it also decomposed the supersaturated solution, precipitating some dicalcium salt and possibly a little of the normal salt in accordance with the equation suggested by Wendt and Clarke: $4CaHPO_4 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2$. The p_H data calculated from the phase-rule data of Bassett (*vide infra*) show that both the di- and the tri-calcium phosphates attain equilibrium with liquid phases whose p_H's are about 5·5 through equilibria involving H_2PO_4' and HPO_4'' ions, the former being in considerable excess. It would be expected, therefore, that a p_H of 5·5 would represent the lowest value to which this downward inflexion could attain, and it is interesting to find that this is about the value shown by Wendt and Clarke's curve. The higher p_H obtained by the author is due to insufficient time being allowed for the attainment of final equilibrium. The earlier appearance of the inflexion in Wendt and Clarke's curve was due to the precipitation of the two phosphates of calcium.

Since this work was completed, Holt, LaMer, and Chown (*loc. cit.*), and Farnell (*loc. cit.*) have described similar increases in hydrogen-ion concentration, whereas Hoffman and Gortner (*loc. cit.*), using a solution of calcium sucrate in order to obtain a calcium solution more concentrated than saturated lime water, found no such variation. They considered that the quantity of sucrose present in their work was such as to be without effect on the hydrogen-ion concentrations. The titration curve of phosphoric acid in presence of sucrose given in Fig. 1 shows that sucrose acts as a buffer in preventing an increase in hydrogen-ion concentration. Wendt and Clarke found, by allowing 10 days for the attainment of equilibrium, that the curve became rectilinear during the addition of the greater part of the second and third equivs. of calcium hydroxide, and indicated hydrogen-ion concentrations varying from p_H 5·5, when a little more than the first equiv. had been added, to p_H 6·0 at 2·5 equivs. This is as would be expected from a consideration of Bassett's work (*vide infra*). Farnell obtained similar results by boiling the solutions and cooling to 20° before measuring the p_H. By allowing the solutions to stand over-night in stoppered bottles, the author found that the change in hydrogen-ion concentration was gradual and varied from p_H 5·98 at 1·53 equivs. to p_H 6·52 at 2·5 equivs. These precipitations had not, however, become complete.

The considerable amount of supersaturation, with its consequent effect on the hydrogen-ion concentration, which occurs when alkaline earths are added to phosphoric acid solutions, renders it difficult to ascertain, by a titration method, when a precipitate should begin to separate. The p_H at which calcium begins to separate as a phosphate is of some importance in the chemistry of soils, and therefore certain data relating to the ternary system $CaO–P_2O_5–H_2O$ obtained by Bassett (J., 1917, **111**, 624; *Z. anorg. Chem.*, 1908, **59**, 1) at 25° and by Cameron and Bell (*J. Amer. Chem. Soc.*, 1905, **27**, 1512) have been studied with respect to the stage of neutralisation of the phosphoric acid in the liquid phases; then, either by comparison with the neutralisation curve (Fig. 1), or by calculation,* an approximate estimate has been made of the hydrogen-ion concentrations of the liquid phases in equilibrium with solid phases containing varying amounts of phosphate. Table II was compiled from Bassett's data, the product $[Ca^{\cdot\cdot}][HPO_4'']$ having been calculated on the assumption that both the mono- and the di-calcium phosphate in solution were completely ionised, an assumption which probably only holds for the very dilute solutions, but which, nevertheless, permits of a satisfactory computation for other solutions. The ionic products $[Ca^{\cdot\cdot}]^3[PO_4''']^2$ are approximate and were calculated from the hydrogen-ion concentrations, the concentration of HPO_4'' ions, and $K_3 = 2{\cdot}7 \times 10^{-12}$.

It will be seen from the table that those liquid phases which contained 0·149% P_2O_5 (= 0·02M-H_3PO_4) or less, as a rule contained calcium hydroxide sufficient to neutralise about 5% of the second stage, giving hydrogen-ion concentrations of the order of $10^{-5\cdot5}$. The amount of lime became in excess of 2 equivs. for liquid phases containing less than 0·00613% P_2O_5 (= 0·0009M-H_3PO_4). The solid phases which were more basic than $CaHPO_4$ are indicated by the molar ratio PO_4/CaO, which is 0·67 for tricalcium phosphate and 0·60 for the substance, hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$. The values of the ratio suggest that the solid phases in equilibrium with the most dilute liquid phases were hydroxyapatite, whereas the ratios corresponding to the more concentrated liquid phases fall, with one exception, between 0·66 and 0·95, proving that the solid phases were either mixtures of tri- and di-calcium phosphate, or possibly dicalcium phosphate in various stages of decomposition. The presence of two solid phases *in equilibrium* with variable liquid phases is incompatible with the phase rule, and it is considered that the conversion of dicalcium phosphate into the normal salt is very slow owing to the ionic requirements of the one being set up simultaneously with those of the other. Consequently, the solid phases may have been indefinite

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* The calculation was based on $[H^{\cdot}] = (100 - x) \times 1{\cdot}4 \times 10^{-7}/x$, where x = the % of neutralisation of the second stage, K_2 being assumed to be the same at 25° as at 20°.

TABLE II.

Analysis of Bassett's data of the system $CaO–P_2O_5–H_2O$.

%CaO.	$\%P_2O_5$.	Solid phase.	% Neutralised.*	p_H.	$[Ca^{\cdot\cdot}][HPO_4'']$ × 10^6.	$[Ca^{\cdot\cdot}]^3[PO_4''']^2$ × 10^{25}.
1·181	3·613	$CaHPO_4$.	83 (I)	3 apprx.	—	—
0·826	2·387	,,	81 (I)	3 ,,	—	—
0·165	0·417	$CaHPO_4$ and $CaHPO_4,2H_2O$.	0·04 (II)	—	5·9	—
0·0696	0·178	$CaHPO_4,2H_2O$.	99·6 (I)	—	—	—
0·0617	0·149	,,	5·1 (II)	5·6	11·7	13
0·0507	0·121	,,	6·3 (II)	5·7	9·7	16
0·0485	0·119	,,	3·3 (II)	5·4	4·9	1·0
0·0427	0·105	,,	3·1 (II)	5·4	3·5	0·4
		PO_4/CaO in solid phase.				
0·0406	0·0980	0·76	5·1 (II)	5·6	5·1	2·0
0·0389	0·0947	0·79	4·1 (II)	5·5	3·8	0·8
0·0373	0·0897	0·95	5·5 (II)	5·6	4·6	1·6
0·0326	0·0777	0·62	6·4 (II)	5·7	4·1	1·6
0·0299	0·0727	0·67	4·4 (II)	5·5	2·4	0·2
0·0269	0·0607	0·66	12·4 (II)	6·0	5·1	7·9
0·0191	0·0465	0·70	4·1 (II)	5·5	0·9	0·02
0·0175	0·0423	0·71	4·9 (II)	5·6	0·9	0·05
0·0174	0·0414	0·69	6·5 (II)	5·7	1·2	0·08
0·0167	0·0405	0·69	4·6 (II)	5·5	0·8	0·01
0·0126	0·0332	—	96 (I)	—	—	—
0·0122	0·0302	0·66	2·4 (II)	5·2	0·2	0·0003
0·00893	0·0196	0·63	12·0 (II)	6·0	0·4	0·03
0·00582	0·0134	0·62	10·1 (II)	5·9	0·2	0·002
0·00600	0·00613	0·62	4·9 (III)	11 apprx.	—	—

* The Roman numerals (I), (II), and (III) relate to the first, second, and third stages, respectively.

and unstable mixtures, although it appeared, as far as could be ascertained experimentally, that equilibrium had been established. The foregoing explanation appears to be valid, for if the solubility product of dicalcium phosphate be assumed to be 5×10^{-6} (approx.), and that of the tricalcium salts to be about 1×10^{-25}, then it is evident from the table that for many liquid phases the two stipulated conditions prevailed at the same time. The decrease in the ionic product of the tricalcium salt (shown by the last few values in the last column) to less than the probable value of the solubility product, 1×10^{-25}, may have been due to the formation of a basic phosphate.

The p_H data given in Table II are of interest on account of their bearing on the reactions which take place in soils when treated with phosphatic fertilisers. If the p_H of the "soil solution" falls below 5·5, the calcium phosphate in the soil will pass into the soluble state, though when in this condition there will be a great tendency for some of the phosphate to suffer "reversion" through reaction with colloidal alumina, but when lime is added so as to raise the p_H to 5·5 and above, the phosphate begins to become insoluble, initially as the dicalcium salt, and finally as the basic phosphate. It would appear that these changes in the composition of the insoluble calcium phosphate can take place without any great diminution in the acidity of the soil. The p_H, 5·9, attained when the PO_4/CaO ratio in the solid phases had become 0·62, confirms Bassett's observation that hydroxyapatite can exist in faintly acid as well as in neutral or alkaline solutions, and that it can probably exist permanently in soils under ordinary conditions, for any di- or tri-calcium phosphate which may first be formed will ultimately become decomposed.

Soil solutions in equilibrium with the dicalcium phosphate contain relatively large amounts of partly neutralised phosphoric acid which, when removed either by "reversion," by the plant, or by drainage, will cause the solid phases to decompose and eventually to become basic without any great change in p_H taking place. The conversion of the phosphate into the insoluble basic state renders it unavailable to the plant. Thus Gedroiz (*Zhur. Opit. Agron.*, 1911, **12**, 529) found that tricalcium phosphate gave the best immediate results on soils not saturated with bases. The necessity of having the soil just on the acidic side of neutrality has recently been emphasised by von Wrangell (*Landw. Vers.-Stat.*, 1920, **96**, 1), who recommends the use of "physiologically acid fertilisers," such as ammonium sulphate, to render any phosphate available.

Series II.

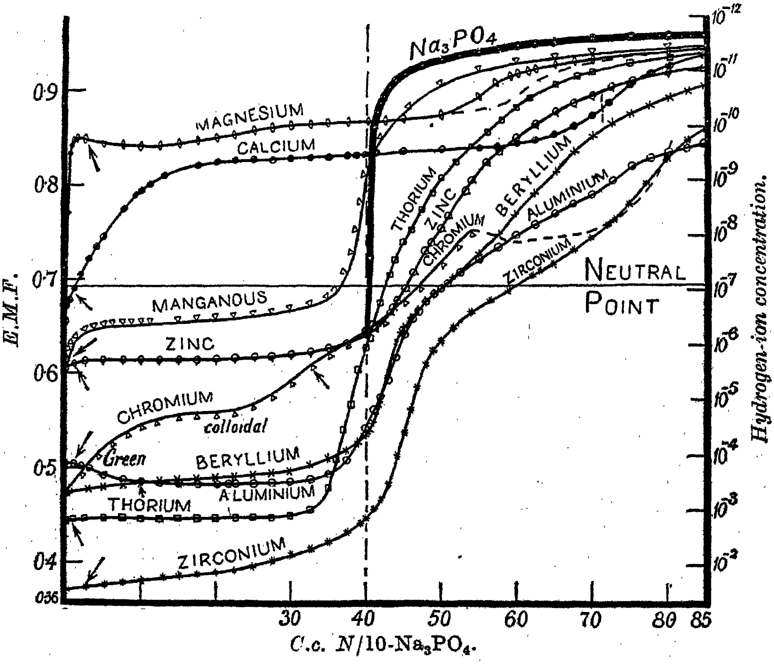
The variation in hydrogen-ion concentration which occurred at 20° when a *N*/10-solution of trisodium phosphate was added to 100 c.c. of the salt solutions (Table III) was followed electrometrically. The *E.M.F.*'s were reproducible, except in the final stages of the chromium and magnesium titrations. Table III also contains the p_H's at which the phosphate precipitates began to separate, and, for purposes of comparison, the respective hydroxide p_H's.

TABLE III.

Solution titrated.	Phosphate p_H.	Hydroxide p_H.
0·02M-$MgSO_4$	9·76	10·49
0·0358M-$CaCl_2$	7·00	—
0·02M-$MnCl_2$	5·76	8·43
0·02M-$ZnSO_4$	5·66	5·20
0·00667M-$Cr_2(SO_4)_3,K_2SO_4$	$\begin{Bmatrix} 4·62 \\ 5·65 \end{Bmatrix}$	5·34
0·00667M-$Al_2(SO_4)_3$	3·79	4·14
0·02M-$BeSO_4$	3·41	5·69
0·01M-$ThCl_4$	2·72	3·51
0·01M-$ZrCl_4$	1·57	1·86

The curves showing the hydrogen-ion concentrations acquired when increasing amounts of trisodium phosphate had been added are given in Fig. 2. The amount of trisodium phosphate required to form the normal metallic phosphate was 40 c.c. in every case except that of calcium chloride, in which it was 71·6 c.c. The curve marked Na_3PO_4 was obtained by adding *N*/10-sodium phosphate solution to 140 c.c. of solution (*i.e.*, the volume attained in the precipitation reactions when stoicheiometrical amounts of the phosphate solution had been added) containing an amount of sodium chloride equal to the amount of neutral salt formed in the precipitation reactions with 40 c.c. of sodium phosphate. It would therefore represent the variation in hydrogen-ion concentration on

FIG. 2.



C.c. *N*/10-Na_3PO_4.

adding an excess of the reactant, if the pure normal phosphates had been precipitated, leaving in solution amounts of phosphate so small as to exert no " buffer action." The arrows denote the beginning of precipitation.

In no instance did the curve corresponding to an excess of the reactant coincide with this curve, the two nearest being those of manganese and calcium. The others are widely divergent. The p_H data given in Table III show that the phosphate precipitates, with the exception of that of zinc, separated from solutions whose hydrogen-ion concentrations were greater than those requisite for the precipitation of the corresponding hydroxides; and thus it appears that, whilst it may be possible to obtain the normal phosphates by the use of an amount of trisodium phosphate insufficient to give complete precipitation, yet as soon as sufficient reactant has been added to bring the p_H of the solution to that necessary for the precipitation of the hydroxide, any metallic salt remaining in solution will then be precipitated, and, moreover, there will be a strong tendency for the precipitate to be decomposed. That some such reaction must have taken place is evident from the curves. The depression of the manganese and the calcium curves must have been caused by the "buffer action" of the added sodium phosphate on the HPO_4'' ions, which had been supplied to the solutions by the precipitates. The greater hydrogen-ion concentrations set up in the zinc, beryllium, aluminium, and thorium reactions were, as may be seen from the sodium hydroxide curve in Fig. 1, of the same magnitude as those produced in the second, and subsequently the third, stage of neutralisation. Hence the precipitates must have decomposed to furnish the mother-liquor with H_2PO_4' ions, some of which, by reacting with the added phosphate, became converted into HPO_4'' ions.

No inflexion occurred in the zirconium chloride reaction when the stoicheiometrical quantity of sodium phosphate had been added, though one appeared on the addition of a small excess. By comparing the range of hydrogen-ion concentrations produced during the addition of this excess with that obtained towards the end of the neutralisation of the first stage of phosphoric acid (Fig. 1), it will be seen that the equilibria which produce these relatively large concentrations of hydrogen ions involve some free phosphoric acid. This must have been liberated through the extreme weakness of zirconium hydroxide, with the result that a highly basic zirconium phosphate was precipitated, the formation of which might have been inferred from the fact that zirconium chloride solutions are very considerably hydrolysed. Thus it was found (Britton, J., 1925, **127**, 2133) that a freshly prepared solution of the concentration used in this titration was hydrolysed to the extent of 54%, and consequently the free acid liberated an equivalent amount of phosphoric acid on reacting with trisodium phosphate. The middle point of the first inflexion (corresponding with the addition of 45 c.c., an excess of 5 c.c.) represents the stage when the liberated phosphoric acid had reacted with the added phosphate to form monosodium phosphate, in accordance with the equation $Na_3PO_4 + 2H_3PO_4 = 3NaH_2PO_4$, from which it follows that the excess of 5 c.c. reacted with twice the amount, *i.e.*, 10 c.c., of phosphoric acid. The total amount of phosphoric acid was equivalent to 40 c.c., and of this 13·3 c.c. corresponded to the first stage of dissociation. The amount of phosphoric acid which had escaped precipitation was therefore 10/13·3 of the quantity required for the normal phosphate of zirconium, and hence the composition of the precipitate might be represented as $6ZrO_2,P_2O_5$. The curve obtained on adding a further excess of the reactant, instead of being sharply inflected through p_H 9 owing to the complete formation of disodium phosphate, showed that a considerable " buffer action " occurred between p_H 6 and 10. It appears, therefore, from the expression $[H^{\cdot}] = K_2[H_2PO_4']/[HPO_4'']$ governing the hydrion concentrations during the second stage of neutralisation, that the precipitate itself, in being decomposed, must have exerted some buffering action by imparting to the mother-liquor a small but continuous concentration of H_2PO_4' ions.

The precipitation curve of aluminium phosphate is interesting in that the first addition of sodium phosphate caused an increase in the concentration of hydrogen ions, reaching a maximum at p_H 3·43 with 17·5—20 c.c. The precipitate became very basic when an excess of sodium phosphate was added as shown by the comparatively large buffering effect—at 80 c.c. the p_H was 9·41; at 100 c.c., 10·02; at 120 c.c., 10·24; and at 140 c.c., 10·33. The hydrolysis of the precipitate into aluminium hydroxide was accompanied by its gradual dissolution in the sodium phosphate solution. Thus the solution became translucent with 80 c.c. and quite clear with 140 c.c. Reference to the hydrogen-ion concentration curve showing the action of alkali on aluminium sulphate solution (Britton, J., 1925, **127**, 2121) shows that sodium aluminate began to form when the p_H became between 9 and 10. Hence it appears that the dissolution of the precipitate in an excess of sodium phosphate was due to the formation of sodium aluminate, the necessary free alkali being furnished by the trisodium phosphate through the exceptional weakness of phosphoric acid in its third stage of ionisation and the resulting hydrolysis of its sodium salt. The inability of disodium phosphate, when added in excess, to cause the precipitate to dissolve is due to the low p_H which it sets up. An excess of this precipitant reduces the hydrogen-ion concentration considerably below that at which aluminium hydroxide becomes precipitable, causing the precipitate to hydrolyse. Thus Munroe (*Amer. J. Sci.*, 1871, [iii], **1**, 329) found that a precipitate, $AlPO_4,Al(OH)_3,2{\cdot}5H_2O$, was obtained when an alum solution was treated with an excess of the disodium salt.

The ease with which aluminium phosphate becomes decomposed on decreasing the hydrogen-ion concentration, even though the reagent used may itself be a soluble phosphate, throws some light on the manner in which vegetation obtains its phosphorus from the soil. When a soluble phosphatic fertiliser, such as superphosphate of lime, is added to a soil, and especially if the soil be sour, "reversion" of the phosphate occurs through the formation of insoluble phosphate on the surfaces of the colloidal particles of hydrated alumina and ferric oxide (see, *e.g.*, Lichtenwalner, Flenner, and Gordon, *Soil Sci.*, 1923, **15**, 157; Hall and Vogel, *ibid.*, p. 367). Marais (*ibid.*, 1922, **13**, 355), in a study of the application of aluminium phosphate as a fertiliser, concluded that, in spite of its low solubility in citric acid, it is of service in soils well stocked with lime, but should never be used on acid soils unless lime is applied in intimate contact with it. Slaked lime causes aluminium phosphate to decompose with the formation of soluble calcium phosphate until p_H 5·5 is reached.

In the author's earlier papers, stress was laid on the remarkable property of beryllium and chromium in forming "soluble basic salts," and attempts have been made to trace any effects that this factor may have on the reactions of the salts of these metals. Precipitation of the basic chromate, carbonate, and borate did not occur until comparatively large amounts of precipitant had been added, and considerable changes in hydrogen-ion concentration had taken place (J., 1925, **127**, 2120; 1926, 125). Although precipitation did not take place from the beryllium sulphate solution until 7·5 c.c. of sodium phosphate had been added, the delay was not accompanied by any great change in hydrogen-ion concentration. As mentioned above, the beryllium precipitate was a basic phosphate. Bleyer and Müller (*Z. anorg. Chem.*, 1913, **79**, 263) assigned the formula $BeO,2Be_3(PO_4)_2,13H_2O$ to a precipitate similarly obtained.

In the chromium sulphate titration, however, the effect was pronounced. At first the sodium phosphate merely caused the violet solution to turn green—a point of importance in connexion with the question of the colours of chromium salt solutions, and one which has always been observed whenever a violet chromium salt solution has been rendered basic (*loc. cit.*). Simultaneously an appreciable decrease in hydrogen-ion concentration occurred until 12 c.c. (= 0·90 equiv. per atom of Cr) had been added, $p_H = 4·62$, a cloudiness then being observed. For the next 10 c.c. the p_H remained nearly constant, although the solution became more and more colloidal, and thereafter a steady rise in p_H occurred, coagulation taking place at p_H 5·65 with 32·5 c.c. (= 2·44 equivs.). The bulk of the precipitate was green and flocculent, but it contained a small quantity of a violet crystalline precipitate, apparently the normal chromium phosphate. The delay in precipitation is significant, as also is the fact that when it took place the hydrogen-ion concentration of the mother-liquor was not very far from that at which chromium hydroxide is precipitated, *viz.*, p_H 5·3. The diminution in hydrogen-ion concentration was gradual until 54 c.c. (= 4·05 equivs.) of sodium phosphate had been added, $p_H = 8·07$, at which stage the *E.M.F.*'s not only became very unsteady, but also showed a remarkable increase in hydrogen-ion concentration. The changes which took place immediately after the addition of each new amount of sodium phosphate are shown by the broken line. The hydrogen-ion concentration subsequently grew smaller, such that when 80 c.c. had been added the p_H had become 9·71. Precipitation became complete just after the stoicheiometrical amount of sodium phosphate, 40 c.c., had been added. The change in p_H with the excess of reactant shows that a basic phosphate had been precipitated, and the exceptional change after 4 equivs. of sodium phosphate had been added indicates that the precipitate underwent rapid hydrolysis. The p_H, 8·07, attained when this change began was that which would have been produced by a solution of phosphoric acid neutralised by caustic soda almost to Na_2HPO_4, *i.e.*, in the present reaction, according to the equation $2Na_3PO_4 + H_3PO_4 = 3Na_2HPO_4$. Hence the equivalent which was in excess of the amount necessary to form the normal chromium phosphate required approximately one-sixth of a molecule of phosphoric acid to bring the p_H of the solution up to about 8, and therefore the amount of phosphoric acid in combination with the precipitate at that stage was about five-sixths of that present in the normal phosphate. It has been suggested (J., 1925, **127**, 2120) that in the ordinary violet chromium salts approximately one equiv. of acid radical exists in a looser kind of combination than do the other two equivs., so that chromium sulphate in solution might be represented as $Cr_2(SO_4)_2(OH)_2$---H_2SO_4, and therefore on treatment with trisodium phosphate the first reaction to take place would be the replacement of this loosely bound molecule of sulphuric acid by two-thirds of a molecule of phosphoric acid, and unless the solubility-product requirements of the normal chromium phosphate are simultaneously satisfied no precipitation would ensue, although a change in hydrogen-ion concentration would be produced, comparable with that set up in the reactions of chromium salts which involve the precipitation of basic salts.

The p_H, 5·66, at which the zinc phosphate precipitate began to form was a little higher than that required by zinc hydroxide, *i.e.*, 5·20, but reference to the hydroxide precipitation curve (Britton, J., 1925, **127**, 2125) shows that the p_H during the main part of the precipitation was 6, whereas the phosphate curve shows a slightly lower p_H, *viz.*, 5·7.

The *E.M.F.*'s recorded in the reaction with calcium chloride up to the addition of 7 c.c. of sodium phosphate tended to be low initially but slowly increased to steady values; for larger volumes of sodium phosphate the voltages given primarily appeared to be reproducible. The stoicheiometrical amount of sodium phosphate was 71·6 c.c., and this, as seen from the curve, gave rise to a hydrogen-ion concentration which was represented by a point of the inflexion corresponding to the completion of precipitation as the normal calcium phosphate. The greater part of the precipitation occurred between p_H 9·5 and 10 and, as will be seen from the sodium hydroxide titration curve (Fig. 1), such a p_H corresponds to equilibria involving a predominance of HPO_4'' and very few PO_4''' ions, thus $HPO_4'' + OH' \rightleftharpoons PO_4''' + H_2O$, which must have been given by the hydrolysis of the tricalcium phosphate into the dicalcium salt: $Ca_3(PO_4)_2 + 2H_2O = 2CaHPO_4 + Ca(OH)_2$. The difference between the p_H's which prevailed during the precipitation of calcium phosphate in series I and II was due to suppression of the hydrolysis in the former case by the presence of a small amount of partly neutralised phosphoric acid, whereas this was absent in the double decomposition. There is, however, very little difference in the p_H's of precipitation of the phosphates of the weaker base-forming metals, *e.g.*, zinc and cobalt.

The precipitation from the magnesium sulphate solution is of interest for two reasons. First, the inflexion indicating the end of precipitation did not appear when the stoicheiometrical amount of sodium phosphate had been added, *viz.*, 40 c.c., but occurred with about 1½ times that quantity. Secondly, the solution from which the precipitate had separated was even more alkaline than that in the calcium reaction, the p_H at which the precipitate began to form being 9·76. The exact incidence of the inflected part depended on the efficiency of agitation of the reaction mixture and on the time allowed before measuring the *E.M.F.* The broken line was obtained by allowing longer time, and the inflexion began at 60 c.c., whereas the first curve was undergoing inflexion with that amount. A p_H of 9·76 must have been produced by the same kind of ionic equilibria as in the calcium phosphate precipitation, in which, however, there was a greater proportion of phosphate ions. The amount of sodium phosphate required to effect precipitation suggests the reaction $MgSO_4 + Na_3PO_4 = MgHPO_4 + NaOH + Na_2SO_4$, but the fact that the p_H remained almost stationary at 10 throughout the course of precipitation shows that the concentration of free alkali was relatively small. Analyses of the mother-liquors showed that the sodium hydroxide had combined with the precipitated magnesium phosphate in the form of a double phosphate, $MgNaPO_4$, and it was therefore the hydrolysis of this double phosphate into magnesium hydrogen phosphate and sodium hydroxide which determined the p_H throughout the precipitation.

Note on the Phosphate Separation.

The observations made in the course of these electrometric titrations afford a satisfactory explanation of the procedure adopted in qualitative analysis for the removal of phosphates. The phosphate precipitation p_H's are functions of the concentrations of both the metallic and the phosphate ions, and the use of dilute solutions tends to keep the concentrations of both the bases and phosphoric acid comparatively small, and thereby fixes within narrow limits the p_H at which the various phosphates are precipitated as the free acid is gradually neutralised and the solution made alkaline. The hydrogen-ion concentrations which prevailed during the formation of the phosphate precipitates (Fig. 2) are approximately those which would be set up if the phosphoric acid had been present in the solution and was subsequently neutralised with alkali. In the "basic acetate" method of removing phosphates, the solution, before treatment with ferric chloride solution, is buffered at about p_H 5 by the acetic acid and an excess of either sodium or ammonium acetate. Fig. 2 shows that the only phosphates to be precipitated from solutions more acid than p_H 5 are those of zirconium, thorium, aluminium, beryllium, and chromium. Ferric phosphate is also precipitated from very acid solutions. The phosphates and hydroxides which are precipitated from solutions of p_H higher than 5 are those of zinc, manganese, calcium, and magnesium, to which should be added cobalt, nickel, strontium, barium, and many of the rare earths. It appears, therefore, that as the p_H of the phosphate solution is raised to 5, the phosphates precipitated will be, first, ferric, then aluminium, and finally chromium, but if the quantity of phosphoric acid in the solution is inadequate to form any or all of these phosphates, then the acid will combine with the bases in the order in which they are precipitated, and consequently the hydroxides themselves may be precipitated. Hence, by having a quantity of these three bases, and preferably of ferric hydroxide, more than sufficient to combine with the total amount of phosphoric acid present, the phosphate will be completely removed without precipitation of the bases belonging to the subsequent groups. Acetic acid has a marked tendency, owing to the formation of soluble basic acetates, to retain the hydroxides in solution even though the p_H's at which they are normally precipitated may have been exceeded (*vide* Britton, J., 1926, 269). These acetate solutions are, however, completely decomposed on boiling, although long boiling may be necessary if too much acetate be used.

Summary.

(1) The dissociation constants, $K_1 = 0{\cdot}94 \times 10^{-2}$, $K_2 = 1{\cdot}4 \times 10^{-7}$, and $K_3 = 2{\cdot}7 \times 10^{-12}$, at 20°, have been shown to satisfy the hydrogen-electrode titration curve of phosphoric acid by sodium hydroxide.

(2) The hydrogen-electrode curves of phosphoric acid in course of neutralisation by the alkaline earths show that this process at first goes beyond the limits fixed by the very small solubilities of the alkaline-earth phosphates, which later become precipitated, although a considerable time must elapse before equilibrium between the precipitates and the solutions is established.

(3) The presence of sucrose in a phosphoric acid solution prevents the exceptional increase in hydrogen-ion concentration which ordinarily occurs during precipitation with calcium hydroxide.

(4) Calculations from Bassett's data for the system CaO–P_2O_5–H_2O at 25° show that calcium phosphate is not precipitated from solutions which are more acid than p_H 5·5. Probable values for the solubility products of di- and tri-calcium phosphates have been found.

(5) Hydrogen-electrode titrations with trisodium phosphate of salt solutions of zirconium, thorium, aluminium, beryllium, chromium, zinc, manganese, magnesium, and calcium have been described, in which it has been shown that all, except the last two, yield basic phosphates. Magnesium forms a double phosphate with sodium. The redissolution of the aluminium precipitate in an excess of precipitant has been traced to the formation of sodium aluminate.

(6) The importance of the p_H data relating to the precipitation of phosphates has been emphasised in respect of (*a*) the application of phosphatic fertilisers to soils, and (*b*) the removal of phosphates in qualitative analysis.

The author expresses his thanks to the Department of Scientific and Industrial Research for a personal grant, to the Chemical Society for a grant from its Research Fund, and to Professor Philip, F.R.S., for kindly placing facilities at his disposal.

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SOUTH KENSINGTON. [*Received, December 16th, 1926.*]

XCV.—*The Nitration of* m-*Iodophenol.*

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THE investigation of the direct nitration of *m*-iodophenol proceeded on similar lines to the work on *m*-chloro- and *m*-bromo-phenols (J., 1925, **127**, 1599; 1926, 155). 3-Iodo-2-, -4-, and -6-nitrophenols, 3-iodo-4 : 6- and -2 : 6-dinitrophenols, and 3-iodo-2 : 4 : 6-trinitrophenol were prepared, but 3-iodo-2-nitrophenol was obtained from the nitration mixture with difficulty owing to the instability of *m*-iodophenol towards sulphuric acid and oleum and to the tardy mono- but ready tri-nitration of the sulphonic acid produced.

The constitutions of 3-iodo-4- and -6-nitrophenols are determined by analogy with those of the corresponding chloro- and bromo-compounds (*loc. cit.*), by their conversion into 2 : 2′-dinitro- and 4 : 4′-dinitro-5 : 5′-dimethoxydiphenyl disulphides and into 2-nitro- and 4-nitro-5-methoxythioanisoles, respectively (Hodgson and Handley, J., 1926, 543), and also by the conversion of each by nitration into 3-iodo-4 : 6-dinitrophenol, which is converted into 4 : 6-dinitroresorcinol on prolonged boiling with aqueous potassium hydroxide. Since 3-iodo-5-nitrophenol has been described by Hodgson and Wignall (J., 1926, 2077), the constitution assigned to 3-iodo-2-nitrophenol is the only one left for this substance. The constitution of 3-iodo-2 : 6-dinitrophenol follows from its preparation from 3-iodo-2- and -6-nitrophenols, and that of 3-iodo-2 : 4 : 6-trinitrophenol from its formation from all the mono- and both the di-nitro-derivatives.

Owing to the extensive decomposition of *m*-iodophenol by concentrated sulphuric acid and the consequent paucity of 3-iodo-2-nitrophenol, we have been unable to obtain 3-iodo-2 : 4-dinitrophenol. Attempts to substitute an amino-group for the halogen in 3-chloro- or 3-bromo-2-nitrophenol and so provide an alternative method for the preparation of 3-iodo-2-nitrophenol were unsuccessful, although the most drastic conditions were employed. The great stability of the halogen thereby demonstrated is found also in 3-iodo-2-nitrophenol, and in 3-iodo-2 : 4 : 6-trinitrophenol, which readily sublimes from boiling concentrated sulphuric acid. On the other hand, 4 : 6-di-iodo-1 : 3-dinitrobenzene, when boiled with a dilute solution of an alkali hydroxide or carbonate, slowly but completely exchanges the whole of its iodine for hydroxyl.

Unlike the corresponding chloro- and bromo-compounds, 3-iodo-2-nitrophenol does not form a hydrate. This was to be expected, since the hydrate of the chloro-compound is very much more stable than that of the bromo-compound. 2-Chloro-6-nitrophenol also does not appear to form a hydrate. The property, therefore, seems to be peculiar to the 3-chloro- and 3-bromo-2-nitrophenols.

Busch's α- and β-iodonitrophenols (*Ber.*, 1874, **7**, 462), which are stated to be 5- and 6-iodo-2-nitrophenols (Beilstein, "Organische Chemie," II, p. 700), are regarded as impure substances by Roberts (J., 1923, **123**, 2710) and as 3- and 4-iodo-2-nitrophenols by Keimatsu (*J. Pharm. Soc. Japan,* 1924, No. 507, 319). Since all the monoiodo-2-nitrophenols are now available, one of the authors (H. H. H.) is repeating Busch's work with the object of determining the mechanism of iodination in presence of mercury compounds.

EXPERIMENTAL.

m-Iodophenol was prepared by the general method (Hodgson, E.P. 200714) from diazotised *m*-iodoaniline. It loses iodine in the presence of boiling water.

Mononitration of m-*Iodophenol.*

3-*Iodo*-6- *and* -4-*nitrophenols*.—*m*-Iodophenol (21·3 g.), liquefied by alcohol (2 c.c.), was added slowly to a solution, vigorously stirred at 15°, of concentrated sulphuric acid (22 g.) and sodium nitrate (16 g.) in water (40 c.c.). After 2 hours, the tarry mass was removed, washed, and steam-distilled; some iodine accompanied the volatile product, 3-*iodo*-6-*nitrophenol* (3·7 g.), which crystallised from light petroleum in long, yellow needles, m. p. 96° (Found: N, 5·5; I, 47·7. $C_6H_4O_3NI$ requires N, 5·3; I, 47·9%).

3-Iodo-6-nitrophenol forms a scarlet *sodium* salt and a stable, orange-brown *silver* salt. Its *methyl* ether was obtained by boiling a solution of 1 g. of the phenol in aqueous sodium carbonate (1 g. in 40 c.c. of water) with methyl sulphate (1·5 c.c.) for 5 minutes, and steam-distilling the product. The white solid thus obtained crystallised from dilute alcohol in shining plates, m. p. 92° (Found: I, 45·3. $C_7H_6O_3NI$ requires I, 45·5%). The *acetate* was prepared by warming an excess of acetyl chloride with a solution of 3-iodo-6-nitrophenol in glacial acetic acid for a short time on the water-bath. On diluting the mixture with water and cooling it, 3-*iodo*-6-*nitrophenyl acetate* separated in hexagonal plates which, after recrystallisation from acetic acid containing a little acetic anhydride, melted at 95° (Found: I, 41·1. $C_8H_6O_4NI$ requires I, 41·4%). The *benzoate*, which was prepared in the same way as the corresponding chloro-compound, separated from alcohol in colourless needles, m. p. 122°.

The liquid remaining after the steam distillation of 3-iodo-6-nitrophenol was filtered hot from the tarry matter; on cooling, it deposited 3-iodo-4-nitrophenol as a yellowish-white solid, which crystallised from light petroleum in very pale yellow needles, m. p. 124° (Found: N, 5·4; I, 47·6%). The tar solidified on cooling, and on crystallisation from benzene and light petroleum gave a further quantity of 3-iodo-4-nitrophenol (total yield, 10 g.). The *sodium* salt formed amber-coloured needles; the yellow *silver* salt darkened on keeping. The *methyl* ether, prepared as described above for the 6-nitro-isomeride, crystallised from dilute alcohol in cream-coloured needles, m. p. 69—70° (Found: I, 45·2%). The *benzoate* separated from alcohol in long, slender, colourless needles, m. p. 119°. The *acetate* separated from dilute acetic acid in fine, colourless needles, m. p. 73·7° (Found: I, 41·2%).

Oxidation of 3-*Iodobenzoquinone*-4-*oxime*.—A solution of the oxime (1 g.) in water (200 c.c.) containing sodium hydroxide (10 g.) and potassium ferricyanide (10 g.) was kept for 48 hours at room temperature; the dark red colour had then changed to amber. On acidification with dilute sulphuric acid, the solution became green and deposited a voluminous, white precipitate (0·3 g.); ether extracted from the filtrate a further 0·4 g. The product crystallised from benzene in pale yellow needles, m. p. 123° (Found: N, 5·5%), and was 3-iodo-4-nitrophenol. This result proves that the nitrosation of *m*-iodophenol takes place in the 4-position (see J., 1925, **127**, 2260).

3-*Iodo*-2-*nitrophenol*.—*m*-Iodophenol (7·5 g.) was added very gradually to oleum (12 c.c.; 27%), the mixture being cooled after each addition. After 1 hour, the temperature was raised gradually to 70—80° and maintained for 1½ hours. The mixture, which had then become a paste of crystals, was cooled, diluted with concentrated sulphuric acid (10 c.c.), and nitrated with a solution of nitric acid (2·5 c.c.; *d* 1·5) in concentrated sulphuric acid (7·5 c.c.), added at such a rate that the temperature never exceeded 30°. After 2 hours, the whole was poured on ice, and the solution carefully concentrated in a current of steam; iodine was evolved continuously, and from the highly concentrated, extensively decomposed product a yellow oil distilled which was collected in numerous small fractions. The earlier fractions would not solidify and were mixtures of *m*-iodophenol and 3-iodo-2-nitrophenol, but the later ones, on cooling, crystallised in long, yellow needles, m. p. 70—71°. The yield was variable and never exceeded 12%. When the quantity of nitric acid was increased, 3-iodo-2 : 4 : 6-trinitrophenol was the main product with a little 3-iodo-2 : 6-dinitrophenol. Diminution of the quantity of nitric acid resulted in a product which did not solidify and was mainly *m*-iodophenol.

3-*Iodo*-2-*nitrophenol* crystallised from water or light petroleum in bright greenish-yellow, spear-shaped needles, m. p. 73·5° (Found: N, 5·3; I, 47·8. $C_6H_4O_3NI$ requires N, 5·3; I, 47·9%). No formation of hydrate could be detected. The *sodium* salt crystallises in orange needles and the *ammonium* salt in red, rectangular plates which readily hydrolyse; the *silver* salt has a deeper orange-brown colour than its 6-nitro-isomeride and rapidly darkens on keeping. The *methyl* ether prepared in the way described above, crystallises from dilute alcohol in colourless micro-plates, m. p. 82—83° (Found : I, 45·2. $C_7H_6O_3NI$ requires I, 45·5%). The *acetate* separates from dilute acetic acid in colourless cubes, m. p. 102·5° (Found : I, 41·2. $C_8H_6O_4NI$ requires I, 41·4%). Mixed with the 6-nitro-isomeride, it melts at 80°.

Dinitration of m-*Iodophenol.*

3-*Iodo*-4 : 6-*dinitrophenol* was prepared from *m*-iodophenol and from 3-iodo-6- and -4-nitrophenols in the same way as the corresponding bromo-compound (*loc. cit.*, p. 158). It is readily volatile in steam and crystallises from light petroleum in yellowish-white needles and from water in yellowish-white plates, m. p. 98° (Found : N, 9·2; I, 40·7. $C_6H_3O_5N_2I$ requires N, 9·0; I, 40·9%). The *silver* salt formed as a bright yellow, gelatinous precipitate when a neutral solution of the ammonium salt was treated with aqueous silver nitrate; it is moderately easily soluble in ammonia, but readily soluble in boiling water, from which it crystallises in golden needles (Found : Ag, 25·6. $C_6H_2O_5N_2IAg$ requires Ag, 25·9%). The gelatinous form changes to a redder, crystalline variety on keeping.

3-*Iodo*-2 : 6-*dinitrophenol.*—*m*-Iodophenol (5·5 g.) was gradually dissolved in 20 c.c. of oleum (27% SO_3), the mixture being cooled after each addition. After 48 hours, nitration below 0° was effected during 30 minutes with a solution of nitric acid (5 c.c.; *d* 1·5) in oleum (15 c.c.), and 2 hours later the whole was poured on ice, and the deep orange solution steam-distilled. Iodine was evolved and almost at the outset of the distillation the main part of the reaction product, which was 3-iodo-2 : 4 : 6-trinitrophenol, separated and was filtered off. The concentration by steam distillation was then continued, with evolution of iodine, and finally 3-*iodo*-2 : 6-*dinitrophenol* passed over slowly; it separated from the distillate in almost colourless, slender needles which, after recrystallisation from water, dilute acetic acid, or light petroleum, melted at 151—152° (Found : N, 9·2; I, 40·7. $C_6H_3O_5N_2I$ requires N, 9·0; I, 40·9%). 3-Iodo-2 : 6-dinitrophenol is readily turned yellow by ammonia, forms yellow solutions in water and alcohol, and very deep yellow ones with dilute aqueous alkalis. The *silver* salt separates slowly in bright orange-red needles when prepared by the usual method, and is sparingly soluble in ammonia and hot water.

3-Iodo-2 : 6-dinitrophenol was also prepared from 3-iodo-2-nitrophenol and from 3-iodo-6-nitrophenol in the same ways as the corresponding chloro- (*loc. cit.*, p. 1602) and bromo- (*loc. cit.*, p. 159) compounds, respectively.

Trinitration of m-*Iodophenol.*

3-*Iodo*-2 : 4 : 6-*trinitrophenol* was prepared in excellent yield as described above, or by the method used for the preparation of the corresponding chloro-compound (*loc. cit.*, p. 1603). It is not volatile in ordinary or in superheated steam, but sublimes slowly from boiling concentrated sulphuric acid. It crystallises from water, in which it is much less soluble than the corresponding chloro- and bromo-compounds, in almost colourless needles, and from glacial acetic acid in characteristic parallelepipeds, m. p. 197° (Found : N, 11·6; I, 35·5. $C_6H_2O_7N_3I$ requires N, 11·8; I, 35·8%). The substance possesses pronounced sternutatory properties, forms deep yellow solutions in water and alcohol, and is not brominated when its solutions are treated with bromine. The yellow *silver* salt is insoluble in ammonia.

The authors' thanks are due to Mr. J. Nixon for help in the heavy preparative work and to the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December* 31*st*, 1926.]

XCVI.—*Solubility Influences. Part IV. The Salting-out of Aniline from Aqueous Solutions.*

By SAMUEL GLASSTONE, JOAN BRIDGMAN, and WILLIAM R. P. HODGSON.

IN continuation of previous work (Part I, J., 1925, **127**, 2660; Part II, J., 1926, 2935; Part III, *ibid.*, p. 2939) on the "salting-out effect," the influence of various salts on the solubility of aniline in water has now been systematically investigated. It has already been shown that substances which can dissolve in the solute the solubility of which is being determined give abnormal results, and consequently the first stage in the present work involved the examination of the solubilities of various salts and sugars in aniline. The following salts were found to be almost insoluble in aniline at 25° : sodium, potassium, and barium chlorides; sodium, potassium, barium, and strontium nitrates; potassium chlorate, chromate, ferrocyanide, fluoride, acetate, oxalate, carbonate, and hydroxide; sodium, potassium, and magnesium sulphates; ammonium oxalate; and sodium citrate. These substances were all used either alone or in pairs in the quantitative investigation of the "salting-out" of aniline from its aqueous solution. Salts which are hydrolysed to give appreciably acidic solutions could not be used. The following substances were found to be more or less soluble in aniline:

lævulose, glucose, sucrose, lactose; lithium, ammonium, cæsium, and rubidium halides (the fluorides were not examined); sodium and potassium bromides and iodides; ammonium and lead nitrates; copper, zinc, nickel, cobalt, chromium, and cerous sulphates. The last six substances all appear to form addition compounds with aniline; some of these compounds have already been isolated (Tombeck, *Compt. rend.*, 1898, **126**, 967) and the others are now being studied.

EXPERIMENTAL.

The aniline used was obtained by the fractionation of a pure commercial specimen until a portion of constant boiling point was obtained. The salts used were the best commercial products and were, in general, not further purified. The salt solutions were made up by weighing the salt and water; a small quantity of aniline was then added and the mixture was well shaken at a temperature a few degrees above that at which the solubility was being determined. The liquid was then placed in a thermostat at 25° or 50° and allowed to stand until it had become clear. (This procedure was found to be more satisfactory than shaking the mixture at the temperature of the thermostat.) The sample of saturated solution for analysis was removed in a warmed pipette, transferred to a stoppered bottle, and weighed. The amount of aniline present was either estimated directly by the bromine method (Sutton, "Volumetric Analysis," 1924, p. 367), or else the solution was first diluted with water and the aniline distilled in steam; the latter procedure was only adopted when the salts present were likely to interfere with the former method of estimating aniline. Preliminary experiments on the analytical method, in which known weights of pure aniline were used, gave very satisfactory results.

The method of calculating the results was the same as used in previous work (*loc. cit.*); m and w represent the number of g.-mols. of added salt and of water, respectively, required to make a solution which will be just saturated with 1 g.-mol. of aniline at the temperature of the experiment. The so-called "hydration number," n, which is a measure of the salting-out effect of a g.-mol. of the salt, is equal to $(w - w_0)/m$ where w_0, the value in pure water, is 135·7 at 25° and 117·2 at 50°. The hydration numbers have been extrapolated, as before, to infinite dilution of the salt, and the values so obtained, which are often only approximate, are given in parentheses at the bottom of each "n" column. A few results only are given for those alkali halides which were found to be soluble in aniline, in order to show the general tendency in these cases.

Lithium chloride.			Lithium bromide.			Lithium iodide.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*	*m.*	*w.*	*n.*
				25°.				
1·27	145·2	7·5	0·54	*128·2*	—	0·34	*125·7*	—
32·29	342·4	6·0	6·90	*133·1*	—	1·69	*113·3*	—
232·7	843·4	3·0	36·61	*118·8*	—	4·80	*70·9*	—
				50°.				
1·10	125·4	7·5	0·48	*114·0*	—	0·30	*110·2*	—
31·59	297·6	5·7	6·35	122·7	0·9	1·52	*101·5*	—
200·1	725·2	3·0	34·37	*111·4*	—	4·61	*68·0*	—

Sodium chloride.			Sodium bromide.			Sodium iodide.		
				25°.				
0·95	154·2	20·5	0·49	139·6	7·9	0·32	136·4	2·2
3·03	186·7	16·8	1·29	146·3	8·2	0·87	137·3	1·8
8·38	246·8	13·2	3·17	163·2	8·7	1·80	*134·6*	—
19·20	345·7	10·9	18·33	244·0	5·9	10·14	*126·6*	—
73·33	708·2	7·8	59·09	413·5	4·7	31·49	174·2	1·2
		(24)			(?)			(?)
				50°.				
2·66	163·7	17·5	0·44	123·8	15·0	0·28	120·0	9·9
7·44	219·0	13·7	2·80	143·9	9·6	0·76	120·6	4·5
31·82	411·8	7·8	17·15	228·1	6·5	25·52	141·2	0·9
					(18)			(13 ?)

Potassium chloride.			Potassium bromide.			Potassium iodide.		
				25°.				
0·74	148·4	17·2	0·43	140·4	10·9	0·30	137·2	4·9
2·11	166·6	14·6	1·16	146·8	9·5	0·77	*134·5*	—
5·33	199·4	11·9	2·63	156·8	8·0	1·59	*132·1*	—
10·43	245·1	10·5	6·88	174·8	5·7	3·62	*132·3*	—
30·89	383·5	8·0	27·57	273·7	5·0	22·68	139·7	0·2
		(22)						
				50°.				
0·64	129·2	18·7	0·37	121·5	11·5	0·27	119·9	10·1
1·91	150·9	17·6	2·35	140·2	9·8	0·69	119·9	3·9
4·93	184·4	13·6	6·25	162·6	7·3	3·07	*112·4*	—
16·85	278·9	9·6	25·28	251·0	5·3	20·80	128·0	0·5
					(14 ?)			(13 ?)

Rubidium chloride.			Rubidium bromide.			Rubidium iodide.		
				25°.				
1·13	143·2	6·7	0·75	*132·6*	—	0·55	*124·2*	—
7·20	194·6	8·2	3·80	140·6	1·3	2·30	*107·6*	—
39·96	326·8	4·8	19·58	181·5	2·3	5·82	*83·7*	—
				50°.				
1·00	126·7	9·5	0·66	*116·1*	—	0·49	*109·5*	—
6·61	179·1	9·5	3·52	130·2	3·6	2·12	*99·2*	—
38·17	312·8	5·1	18·51	171·5	3·2	5·58	*80·2*	—

Cæsium chloride.			Cæsium bromide.			Cæsium iodide.		
				25°.				
0·74	*132·2*	—	0·56	*126·3*	—	0·50	*116·9*	—
3·59	*134·7*	—	2·37	*111·5*	—	1·71	*98·5*	—
12·68	141·4	0·5	5·86	*84·6*	—	2·60	*69·2*	—
				50°.				
0·66	117·5	0·5	0·49	*110·9*	—	0·44	*105·8*	—
3·41	130·1	3·8	2·21	*104·2*	—	1·52	*87·2*	—
12·75	142·1	2·0	5·92	*85·4*	—	2·54	*67·4*	—

Ammonium chloride.			Ammonium bromide.			Ammonium iodide.		
				25°.				
1·05	140·9	4·9	0·49	*127·1*	—	0·34	*131·7*	—
5·82	155·1	3·3	5·23	*116·0*	—	2·82	*90·9*	—
13·94	162·2	1·9	11·93	*97·1*	—	7·31	*39·2*	—
				50°.				
0·95	127·6	10·9	0·43	*111·8*	—	0·30	*115·7*	—
5·42	144·3	5·0	4·76	*103·5*	—	2·41	*77·6*	—
13·72	163·1	3·3	11·15	*90·7*	—	6·25	*33·5*	—

The following results were all obtained at 25°.

Barium chloride.			Potassium nitrate.			Potassium chlorate.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*	*m.*	*w.*	*n.*
0·26	142·8	28·2	0·50	138·0	4·6	0·20	137·3	7·9
0·48	148·8	27·1	1·34	142·9	5·4	0·42	139·4	8·8
0·59	151·7	27·3	3·04	153·4	5·8	0·63	140·3	7·2
1·37	169·6	24·8	5·33	169·4	6·3	0·86	141·8	7·1
3·88	218·6	21·3	8·31	186·5	6·1	1·11	142·9	6·5
		(29)			(?)			(11·5 ?)

Potassium acetate.			Potassium carbonate.			Potassium hydroxide.		
0·55	146·1	19·0	0·42	157·5	52·2	1·06	159·8	22·8
1·54	160·1	15·8	1·45	211·1	52·0	3·69	218·1	22·4
3·90	191·3	14·2	4·90	338·7	41·4	13·10	367·2	17·7
11·84	257·7	10·3	35·26	1084	26·9	78·28	975·0	10·7
30·04	250·6	3·8	502·9	7199	14·2	1055	6098	5·6
83·14	452·7	3·8			(72 ?)	4083	12730	3·1
		(23)						(29 ?)

Potassium chromate.			Sodium nitrate.			Barium nitrate.		
0·29	150·5	51·7	0·62	143·1	12·5	0·09	*133·8*	—
0·88	176·4	46·3	1·67	150·0	8·5	0·19	136·5	4·2
2·33	225·7	38·7	3·98	167·2	8·1	0·29	138·1	8·1
8·37	380·7	29·3	11·94	225·9	7·6	0·40	139·3	9·0
30·35	764·5	20·7	73·35	519·7	5·2	0·51	140·0	8·5
		(60)			(15 ?)			(?)

Strontium nitrate.			Sodium sulphate.			Sodium citrate.		
0·24	136·2	2·1	0·42	162·4	63·9	0·22	156·9	94·8
0·62	138·4	4·3	1·45	216·3	55·6	0·71	192·2	80·0
1·35	142·7	5·2	4·81	345·8	43·7	2·09	270·2	64·4
3·30	155·0	5·9	13·31	599·4	34·8	9·70	555·6	43·3
11·83	208·4	6·1			(74)	18·99	821·4	36·1
		(?)						(115)

Potassium sulphate.			Potassium ferrocyanide.			Potassium oxalate.		
0·15	145·3	63·1	0·19	183·7	250·2	0·35	155·9	58·2
0·33	155·0	59·0	0·40	171·9	91·0	1·08	189·4	49·7
0·76	177·3	54·5	1·04	213·7	74·8	2·92	245·4	37·6
2·09	232·6	46·3	3·58	334·8	55·6	9·14	422·0	31·3
		(72)			(350)			(70)

Magnesium sulphate.			Ammonium oxalate.			Potassium fluoride.		
0·47	158·0	47·1	0·21	144·5	41·7	1·07	168·9	31·1
1·62	201·7	40·7	0·44	153·4	39·9	3·84	235·7	25·6
5·00	300·2	32·9	0·73	162·3	36·5	14·12	410·6	19·5
30·29	1282	37·8	4·04	171·3	34·3			(35)
		(53 ?)			(46)			

The values of w are given in italics in those cases in which the salt causes the solubility of aniline in water to *increase*, hence it is seen that substances which are soluble in aniline (see p. 636) do not salt it out from its aqueous solution. This behaviour, as was the case with ethyl acetate (see Parts I and II), is most marked with iodides and nitrates, and, in fact, at 25° aniline is miscible in all proportions with a 60% solution of lithium iodide in water (compare Part I, p. 2665). We may assume, as before (Part II, p. 2935), that the "hydration number" of the iodide ion is zero, and so we may calculate the following values for the "hydration numbers" *per equivalent* of various ions at infinite dilution:

"Hydration" of Ions at Infinite Dilution.

Kations.				Anions.							
$Na^{\cdot}$	14	$NH_4^{\cdot}$	3	$Fe(CN)_6''''$	75	C_2O_4''	23	$C_2H_3O_2'$	11	NO_3'	0
$K^{\cdot}$	12	$Sr^{\cdot\cdot}$	3·0	Citrate'''	24	F'	23	Cl'	10	I'	0
$Ba^{\cdot\cdot}$	4·5	$Mg^{\cdot\cdot}$	2·5	SO_4''	24	CrO_4''	18	Br'	5		
				CO_3''	24	OH'	17	ClO_3'	0		

The "hydration numbers" for most of the kations are distinctly unusual even when determined from experiments on salts which are insoluble in aniline; the abnormality may be connected with the basic nature of the aniline, or it may be due to the hydrolysis of the salts, but further discussion is unprofitable in the absence of sufficient information. For anions, however, the values given above bear a striking resemblance to those obtained from the experiments on the salting-out of ethyl acetate from its aqueous solution. It is again seen that, as a rule, high valency and small size tend to increase the salting-out power of an ion. Rothmund ("Löslichkeit," 1907, p. 152) has observed that, in general, the effect of a salt in reducing the solubility of a neutral substance is independent of the nature of the solute, and the results given above, calculated by a different method, show that this generalisation holds good, in a modified form, for the salting-out of ethyl acetate and aniline.

The Salting-out Effect of Mixtures.—The influence on the solubility of aniline of the following mixtures has been examined at 25°: sodium and potassium chlorides, sodium and barium chlorides, sodium and potassium nitrates, sodium and barium nitrates, potassium and barium nitrates, potassium chloride and nitrate, and sodium chloride and potassium nitrate. The results are given in terms of M_1 and M_2, representing the number of g.-mols. of each of the substances in the mixture (in the order named at the head of each table of results) which, when dissolved in w g.-mols. of water, form a saturated solution with 1 g.-mol. of aniline. The values of $w - w_0$ determined experimentally, given in the columns headed "obs.," are compared with those calculated by the *second* method described in Part III of this series (*loc. cit.*). The agreement between the observed and the calculated values of the salting-out powers ($w - w_0$) of various mixtures confirms the conclusion therein reached, that "the salting-out power of a mixture is, in general, equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of the ions."

		$w - w_0$.	
M_1.	M_2.	obs.	calc.
Sodium and potassium chlorides.			
1·41	1·10	37·6	40·9
1·59	2·51	55·8	59·3
3·35	1·33	65·3	67·5
3·77	2·96	84·7	86·8
4·94	7·74	136·6	138·2
10·99	4·31	167·7	169·2
14·49	11·36	241·1	243·5
Sodium and potassium nitrates.			
0·80	0·68	9·6	9·5
0·87	1·48	16·4	13·7
1·77	0·75	18·8	17·9
1·89	1·59	24·7	24·1
2·20	3·70	40·7	40·2
4·48	1·88	46·3	46·9
5·36	4·51	66·8	67·1
Potassium chloride and nitrate.			
0·98	0·74	18·8	18·6
1·04	1·54	23·8	23·5
2·20	0·81	33·0	34·7
2·33	1·72	38·7	39·2
2·71	4·00	55·3	55·2
6·12	2·26	79·9	79·8
7·25	5·35	104·2	103·5

		$w - w_0$.	
M_1.	M_2.	obs.	calc.
Sodium and barium chlorides.			
1·36	0·38	32·2	33·8
1·49	0·84	43·8	46·1
3·25	0·46	59·3	61·7
3·60	1·01	74·3	75·4
4·45	2·50	109·5	108·0
10·53	1·48	154·5	154·5
13·28	3·73	208·8	203·0
Sodium and barium nitrates.			
0·80	0·26	8·4	8·6
0·86	0·61	13·1	11·3
1·75	0·28	16·9	16·4
Potassium and barium nitrates.			
0·66	0·27	5·8	5·4
0·70	0·57	9·6	7·8
1·42	0·28	11·6	9·9
Sodium chloride and potassium nitrate.			
1·32	0·78	27·1	27·5
1·41	1·66	33·4	32·5
3·15	0·91	53·1	53·6
3·36	1·94	60·3	59·9
3·90	4·51	79·6	76·6
9·89	2·86	137·3	136·8
11·7	6·76	167·7	164·9

Owing to the fact that so many common salts are soluble in aniline, it was not found possible to investigate the salting-out power of a complex ion, in order to compare the value with that of its constituents.

Summary.

(1) The solubility of aniline has been determined in aqueous solutions of a number of single salts, and of mixtures of salts.

(2) The results obtained confirm the conclusions reached as the result of previous work on the salting-out of ethyl acetate.

(3) The salting-out effect of anions on the solubility of aniline is almost identical with that on the solubility of ethyl acetate, but the results obtained with some kations are quite different.

UNIVERSITY COLLEGE, EXETER. [*Received, January 20th*, 1927.]

XCVII.—*Studies of Electrolytic Polarisation. Part VI. Electro-deposition Potentials of Alloys of Zinc with Iron, Cobalt, and Nickel.*

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IT has been known for some time (Toepffer, *Diss.*, Breslau, 1899; *Z. Elektrochem.*, 1899, **6**, 342; Küster, *ibid.*, 1900, **7**, 257; Treadwell, *Diss.*, Zurich, 1909, see Foerster, *Z. Elektrochem.*, 1911, **17**, 883; von Escher, *Diss.*, Dresden, 1912, see Foerster, *Z. Elektrochem.*, 1916, **22**, 85; Schoch and Hirsch, *J. Amer. Chem. Soc.*, 1907, **29**, 314) that if a gradually increasing current is passed through a solution containing a mixture of zinc and nickel or iron salts, the initial deposit on the cathode consists mainly of the iron-group metal but contains a small proportion of zinc. If the *C.D.* is increased a point is reached—at very low *C.D.*'s at room temperature, but at much higher *C.D.*'s at higher temperatures—at which the cathodic potential increases rapidly until it attains a value very close to that at which pure zinc would be deposited from a solution of the zinc salt only; the deposit under these conditions contains only a small proportion of nickel or iron. It was considered (Treadwell, *loc. cit.*) that the zinc deposited with the nickel increases the resistance to cathodic deposition which already exists in the case of the latter metal, with the result that a much higher negative potential is required to deposit the nickel; the result of the increased polarisation effect is that the deposit becomes richer in zinc until finally it contains only a small proportion of nickel. The results of von Escher suggested that the intensity of this polarisation depends on the hydrogen-ion concentration of the electrolyte, since the rapid rise of cathodic potential was found to occur more readily in a weakly acid than in a neutral solution of ferrous and zinc sulphates; hence hydrogen ions apparently enhance the retardation effect caused by zinc on the deposition of iron (see Grube, *Trans. Faraday Soc.*, 1914, **9**, 214; Foerster, "Elektrochemie Wässeriger Lösungen," 1922, p. 378).

In view of the results obtained previously on the electro-deposition potentials of iron, nickel, and cobalt, and their alloys (J., 1926, 2887, 2897) in solutions of varying hydrogen-ion concentration, it was of interest to investigate the changes of cathodic potential occurring with increasing *C.D.* in solutions of iron, cobalt, or nickel containing zinc ions, along the lines followed previously. The general observations of previous authors (*loc. cit.*) have been confirmed and found to apply to these solutions. Moreover, it has been found that, as in the case of anodic passivity, the *C.D.* may be reduced considerably below that at which the sudden increase of potential occurs before the corresponding fall of potential results.

EXPERIMENTAL.

Electrolytic Solutions and Electrodes.—The solutions were generally made up by adding the requisite amount of zinc sulphate and either ferrous, cobalt, or nickel sulphate to a sodium acetate–acetic acid buffer mixture such as was used in previous work (*loc. cit.*); the total concentration of zinc and iron-group metal was 1 g.-equiv. per litre. The zinc sulphate was a recrystallised commercial specimen and the other salts were of the same quality as had been used before. The cathodes were of copper covered with a layer of iron, cobalt, or nickel, according to the metal in the electrolyte; the exposed area was generally 7·5 sq. cm. The anode was a short piece of platinum wire, and this was separated from the cathode by means of a porous pot when ferrous solutions were being used.

Potential Measurement.—Owing to the instability of the electrode potential in the vicinity of the *C.D.* at which the rapid increase of negative potential occurred, it was necessary to modify slightly the commutator–extrapolation method used in previous work. Preliminary experiments were made at a number of *C.D.*'s in order to determine the rate of fall of cathode potential in the first 0·012 sec. after the polarising current was switched off. The measurements were extrapolated in the usual way (J., 1924, **125**, 250) so that the potential at the instant of switching off the current could be determined and hence the fall of potential occurring in the first 0·002 sec.; this quantity was determined under a variety of conditions and never exceeded about 0·04 volt. In the actual measurements, the commutator was set so as to give the potential of the electrode at an average time of 0·002 sec. after the polarising current was stopped; the correction, found as described above, for the particular condition of the electrode was then added in order to give the values quoted below; these must be very close to the actual electrode potentials while the current was flowing.

As in previous work, the current passing through the electrolyte was increased or decreased by stages and kept constant for 1 minute before the potential was measured; the reference electrode was in every case a calomel half-element containing a saturated solution of potassium chloride and no allowance was made for liquid-junction potential.

Results.—The potentials recorded in Table I were obtained with a mixture of 0·1 g.-equiv. of zinc and 0·9 g.-equiv. of nickel in solutions of varying hydrogen-ion concentration at temperatures of 15° and 95°. (All *C.D.*'s throughout this paper are expressed in terms of amps. × $10^{-4}/cm.^2$, and potentials are on the hydrogen scale.)

TABLE I.

Cathode potentials in 1Zn : 9Ni solutions.

	$N/50$-H_2SO_4.		p_H 2·8.		p_H 4·0.		p_H 5·5.	
C.D.	15°.	95°.	15°.	95°.	15°.	95°.	15°.	95°.
2·8	−0·19	−0·16	−0·32	−0·18	−0·41	−0·22	−0·47	−0·25
4·2	−0·22	−0·17	−0·41	−0·20	−0·45	−0·23	−0·50	−0·26
8·4	−0·28	—	−0·52	−0·24	−0·52	−0·25	−0·56	−0·30
12·0	−0·44	−0·21	−0·56	—	−0·56	−0·27	−0·79*	−0·32
20·0	−0·56	−0·23	−0·58	−0·28	−0·57	−0·31	−0·79	−0·34
32·0	−0·58	—	−0·60	—	−0·80*	−0·33	—	—
40·0	−0·80*	−0·26	−0·62	−0·31	—	—	−0·80	−0·42*
80·0	—	−0·29	−0·80*	−0·35	—	−0·35	−0·81	−0·43
160·0	−0·82	−0·30	−0·81	−0·37	−0·81	−0·39	—	−0·43
210·0	—	−0·43*	—	—	—	−0·43*	—	—
320·0	—	−0·43	−0·82	−0·38	—	−0·44	−0·83	—
640·0	—	−0·45	—	−0·42*	—	—	—	—
960·0	—	—	—	−0·43	—	−0·45	—	—

The general conclusions to be drawn from these results are that the potential of the electrode after the sudden increase has occurred —marked with an asterisk in Table I—is independent of the hydrogen-ion concentration of the solution, and that this potential rise occurs less readily, *i.e.*, at higher *C.D.*'s, at high temperatures and high hydrogen-ion concentrations.* Before the rapid increase of negative potential, the deposit on the cathode resembles ordinary electrolytic nickel in appearance and is not easily attacked by acids, but the metal deposited at the higher potentials is grey and dull, like electrolytic zinc, and is readily attacked by dilute acids, leaving a black residue of finely-divided nickel. This zinc-rich deposit obtained at 95° appears to contain relatively more nickel than does the corresponding deposit obtained at 15°, in agreement with the change in deposition potential from − 0·43 at 95° to − 0·80 at 15°. It should be noted that the first alloy, rich in nickel, is deposited at a potential of − 0·56 to − 0·58 at 15° and about − 0·30 at 95°; these are roughly the potentials at which pure nickel would be deposited from a solution of nickel sulphate alone at the concentration used in the mixture (J., 1926, 2887).

All these general observations have been confirmed by a large number of potential measurements made on various solutions of zinc sulphate and nickel, cobalt, or ferrous sulphate; it has also been found that the sudden increase of potential occurs at lower *C.D.*'s the greater the proportion of zinc to iron-group metal in the electrolyte. For solutions at the same hydrogen-ion concentration and temperature and containing the same relative proportion of zinc, the zinc-rich alloy is deposited at lower *C.D.*'s in the case of nickel than in that of cobalt. With iron–zinc mixtures the zinc-rich alloy is only obtained at much higher *C.D.*'s; *e.g.*, in a solution of p_H 2·8 containing 1 atom of zinc to 9 atoms of iron (compare Table I), the sudden increase of potential occurs at a *C.D.* of about 210 × 10^{-4} at 15° and 640 × 10^{-4} at 90°. Once this higher potential condition has set in, however, the current may be reduced to very low values, especially at low temperatures, before the corresponding fall of potential is observed.

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* The anomalous result with $N/50$-sulphuric acid is probably due to the solution not being buffered.

In order to compare the results obtained with different solutions, it was considered most satisfactory to determine a potential value equivalent to the deposition potential of the zinc-rich alloy for each solution; the nearest approach to this would be the cathodic potential of the electrode when the alloy was being deposited at the slowest possible rate. The following method was therefore adopted: The polarising current was increased to a fairly high value, so as to cause deposition of the zinc-rich alloy, and then reduced gradually; the potential was measured at each stage and found to decrease very slowly and then to remain almost constant before decreasing suddenly. This constant value was regarded as the deposition potential of the alloy of zinc and the iron-group metal. The observations were repeated at a number of temperatures and the results are summarised in Table II. The potential measurements

TABLE II.

Deposition potentials of zinc-rich alloys.

* Zn %.	15°.	35°.	55°.	65°.	75°.	85°.	95°.
Iron–Zinc.							
2·5	−0·80	−0·78	−0·73	−0·66	−0·58	−0·52	−0·50
5·0	−0·80	−0·79	−0·75	−0·69	−0·59	−0·53	−0·50
7·5	−0·80	−0·79	−0·76	−0·73	−0·69	−0·62	−0·53
10·0	−0·80	−0·79	−0·77	−0·75	−0·73	−0·70	−0·66
50·0	−0·78	−0·78	−0·77	−0·76	−0·75	−0·74	−0·73
Cobalt–Zinc.							
5·0	−0·80	−0·75	−0·68	−0·63	−0·57	−0·50	−0·41
10·0	−0·79	−0·75	−0·70	−0·66	−0·60	−0·52	−0·43
20·0	−0·79	−0·76	−0·72	−0·69	−0·65	−0·59	−0·49
40·0	−0·78	−0·78	−0·76	−0·75	−0·73	−0·70	−0·66
50·0	−0·78	−0·78	−0·77	−0·76	−0·75	−0·73	−0·70
70·0	−0·77	−0·77	−0·77	−0·76	−0·76	−0·75	−0·72
Nickel–Zinc.							
1·0	−0·80	−0·65	−0·55	−0·49	−0·45	−0·40	−0·38
5·0	−0·80	−0·69	−0·59	−0·54	−0·47	−0·41	−0·39
10·0	−0·79	−0·70	−0·62	−0·56	−0·50	−0·44	−0·42
30·0	−0·78	−0·74	−0·68	−0·64	−0·56	−0·49	−0·45
50·0	−0·77	−0·75	−0·72	−0·70	−0·67	−0·61	−0·56
70·0	−0·76	−0·75	−0·73	−0·71	−0·68	−0·63	−0·58
90·0	−0·76	−0·75	−0·74	−0·73	−0·72	−0·70	−0·65

* This gives the zinc in the electrolyte as an atomic percentage of the total zinc and iron-group metal.

were very consistent and, as indicated above, independent of the hydrogen-ion concentration of the electrolyte.

Discussion.

It appears very probable, from the results of the foregoing experiments, that the hydrogen-ion concentration of the electrolyte, contrary to the views of previous authors (see p. 641), plays no direct part in any influence which the simultaneously deposited zinc may have on the retardation of the electro-deposition of the iron-group metals. In general, the sudden increase of cathode potential, and the change in the nature of the deposit from an alloy rich in iron-group metal to one rich in zinc, occur at a lower *C.D.* the smaller the hydrogen-ion concentration of the solution; this is merely due to the fact that a given rate of metal deposition is more easily reached when the solution is less acidic, and not because the hydrogen ions accelerate the deposition of nickel, iron, or cobalt. It is doubtful, too, if the small amounts of zinc deposited with the iron-group metal at the low cathodic potentials appreciably affect the deposition of the latter; for the initial deposition of the alloy poor in zinc occurs almost at the same potential as that at which the iron, cobalt, or nickel itself would be deposited, and, further, if the zinc inhibited the deposition of nickel, we should expect the cathode potential to rise rapidly with increasing *C.D.* from the instant at which metal deposition first occurs, instead of remaining fairly low over an appreciable range of current (see Table I).

An alternative view is the following (nickel is taken as representing any of the three iron-group metals): A small quantity of zinc does not appreciably affect the deposition of the nickel, or, in terms of the views expressed in connexion with previous work (*loc. cit.*), it has no influence on the rate of transformation of metastable to stable nickel, although in the zinc-rich alloy this rate of change is probably affected. The initial deposit at low *C.D.*'s will probably contain relatively more nickel than is present in the solution, and as the *C.D.* is increased gradually the composition of the deposit, as judged from the potential measurements, will not vary appreciably; a point will be reached, however, at which the nickel ions cannot diffuse towards the electrode as fast as they are being deposited. In order to maintain the current, an increased proportion of zinc ions must be discharged and an alloy richer in zinc commences to be deposited; owing to the high overvoltage of hydrogen at a zinc electrode it is fairly certain that hydrogen evolution at this new deposit will be retarded, with the result that the efficiency of metal deposition is increased and still more zinc must be deposited. This process results in the rapid increase in the proportion of zinc in the deposit and corresponds with a rapid rise in the cathodic potential almost up to that at which pure zinc is deposited; the deposit now consists of an alloy very rich in zinc and rarely contains more than about 20% of iron-group metal. Further increase in the *C.D.* should result in a much more gradual increase in the zinc content of the deposit, and at very high *C.D.*'s this may even decrease slightly owing to the depletion of the electrolyte in the vicinity of the cathode. It might be anticipated that at this point, or as a result of decreasing the *C.D.* whereby the solution near the cathode would once more contain a large proportion of nickel, the original process of the deposition of a nickel-rich alloy would recommence; this does not occur, however, and it is concluded, therefore, that in the zinc-rich alloy the change from metastable to stable nickel is considerably retarded, and so the latter metal cannot be deposited at its ordinary potential. On decreasing the *C.D.* far below the point at which the sudden increase of potential occurred, a corresponding fall is observed; this cannot be due to any change in the concentration of the electrolyte near the cathode because the current value is generally so low that diffusion cannot play any appreciable part, and the "diffusion layer" must be almost identical with the bulk of the electrolyte. The suggested explanation for the fall of potential is that on reducing the *C.D.* the deposit becomes richer in nickel, and consequently the hydrogen overvoltage steadily decreases until a point is reached at which discharge of hydrogen ions can occur so readily that the discharge of zinc ions is no longer necessary to maintain the flow of current. A smaller proportion of zinc in the deposit will cause the hydrogen overvoltage to fall still further and so the cathode potential falls fairly rapidly to a low value at which almost all the current results in the discharge of hydrogen ions, although a small amount of nickel may also be deposited.

At increased temperatures, the rate of diffusion of the electrolyte is increased and the hydrogen overvoltage is decreased, hence the rapid rise in potential occurs at a higher *C.D.* than at low temperatures. Since the normal rate of change of metastable to stable nickel is greater at high temperatures, it is to be expected that the zinc-rich alloy will contain relatively more nickel than at low temperatures; the deposition potentials, in accordance with this, are in most cases much lower than that at which pure zinc is deposited (see Table II; the deposition potential of pure zinc from a *N*-solution at 95° was found to be − 0·74 volt).

A close examination of Table II reveals a number of points of interest which cannot be discussed owing to lack of information on the nature and properties of the individual deposits, obtained at different temperatures, from various solutions containing zinc and either iron, cobalt, or nickel.

Summary.

(1) It has been confirmed that during the electrolysis of a solution containing a mixture of zinc and nickel or iron the cathodic potential at some point rises rapidly and an alloy consisting mainly of zinc is deposited; the same phenomenon has also been observed with solutions of cobalt and zinc.

(2) The current density at which the sudden increase of potential occurs is generally smaller the lower the temperature, the greater the proportion of zinc in the solution, and the lower the hydrogen-ion concentration.

(3) The deposition potential of the zinc-rich alloy has been measured in solutions containing various proportions of zinc and iron, cobalt, or nickel at temperatures ranging from 15° to 95°; this potential decreases with increasing temperature.

(4) The theories of previous authors do not appear to explain adequately the results of the present work, and alternative suggestions have been made; the sudden increase of cathodic potential is attributed to a decrease in the concentration of the nickel, cobalt, or ferrous ions in the vicinity of the cathode, with the result that an alloy richer in zinc and with a high hydrogen overvoltage is deposited.

UNIVERSITY COLLEGE, EXETER. [*Received, February 9th,* 1927.]

XCVIII.—*The Molecular Conductivity of Cadmium Iodide in Acetonitrile.*

By FREDERICK KARL VICTOR KOCH.

CADMIUM iodide is of especial interest from the electrochemical point of view since both of its constituent elements show considerable residual valency in their compounds. The solutions of this salt therefore contain highly complex molecular and ionic species and have been the subject of considerable investigation (McBain, *Z. Elektrochem.*, 1905, **11**, 215).

The following results for the molecular conductivity of this compound in acetonitrile at 0° and 25°, and the calculated values of the temperature coefficients, not only furnish additional evidence of this complexity, but also allow certain general conclusions to be drawn as to the molecular state of cadmium iodide in these solutions.

Apparatus and Materials.—The bridge used was of the drum type (Leeds and Northrup) and was 10 m. long, whilst the standard resistances were of the dial pattern (Cambridge and Paul). The alternating current was supplied by a valve oscillator, electromagnetically shielded from the rest of the apparatus. A variable condenser was placed in parallel with the standard resistance to balance the capacity of the conductivity cell. An excellent minimum was found (usually complete silence) and the readings could therefore be obtained with a high degree of accuracy.*

The conductivity cell was of the cylindrical type with vertical grey platinum electrodes and a ground-in stopper (Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431). The cell constant was determined by the method of Parker and Parker (*ibid.*, 1924, **46**, 312).

Acetonitrile (B.D.H.) was allowed to stand over solid potash for 2 or 3 days in order to remove acetic acid and moisture. It was then decanted on to calcium chloride and, after distillation, shaken with a very little phosphorus pentoxide for about a day. After a final distillation from the phosphorus pentoxide the product (b. p. 81·6°/760 mm.) had a specific conductivity of 0·5—1·0 × 10^{-7} mho (Walden gives $\kappa = 0{\cdot}398 \times 10^{-6}$ mho).

Cadmium iodide (Analytical Reagent) was purified from iodine (which it contained in sufficient quantity to give yellow solutions in acetonitrile) by recrystallisation—once from conductivity water and twice from absolute alcohol. It was then dried over phosphorus pentoxide in a vacuum. Solutions of pure cadmium iodide in acetonitrile are colourless.

The most concentrated solution (approx. *N*/10) was made up by weight and the others, except the last three, by volume-dilution.

The following table, giving the specific conductivities of three of the intermediate solutions at 0°, which were made up by dilution from two different stock solutions of the same concentration, indicates the reproducibility of the results. (*V* indicates the volume of solvent containing 1 g.-mol. of cadmium iodide.)

	κ (mho).	
V (litres).	(1).	(2).
163·4	1·842 × 10^{-4}	1·858 × 10^{-4}
326·7	0·943 ,,	0·948 ,,
653·4	0·483 ,,	0·480 ,,

For the majority of the solutions, the error in Λ (which was calculated from the average specific conductivity) is estimated to be not greater than 0·5%. The values of Λ in the case of the three most dilute solutions are probably somewhat less certain owing to the increasing significance of the specific conductivity of the pure solvent.

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* The author is indebted to Mr. A. R. Martin for the set-up and loan of the conductivity apparatus.

The values for the density of acetonitrile used in calculating the dilutions were 0·8052/0° (Beilstein) and 0·7800/25° (this investigation).

The temperature coefficients are calculated by using the molecular conductivities at 0° and 25° of the same original solution, *i.e.*, a solution of the same weight-normal concentration.

At 0° ± 0·01°.			At 25° ± 0·01°.		
V (litres).	$\kappa \times 10^4$.	Λ.	*V* (litres).	$\kappa \times 10^4$.	Λ.
*10·21	24·05	24·57	*10·53	24·46	25·75
20·42	13·15	26·86	21·06	12·98	27·33
40·84	6·950	28·38	42·12	6·713	28·29
81·68	3·612	29·48	84·24	3·426	28·85
163·4	1·850	30·23	168·5	1·736	29·23
326·7	0·9454	30·87	337·0	0·8842	29·80
653·4	0·4815	31·46	673·9	0·4524	30·50
1321	0·2510	33·16	1363	0·2519	34·34
2696	0·1455	39·23	2788	0·1526	42·54
7816	0·05425	42·40	8069	0·06194	49·98

* Determination of the density of an approx. *N*/10-solution of cadmium iodide in acetonitrile has shown that if the dilution is expressed in terms of volume of solution instead of volume of solvent, the first values of Λ in the above table would both be increased by about 0·5%.

The temperature coefficients of the molecular conductivity calculated from the above data are: + 0·00192, + 0·000750, − 0·000127, − 0·000855, − 0·00132, − 0·00139, − 0·00122, + 0·00142, + 0·00338, and + 0·00715, for the ten dilutions, respectively.

The significant point is that the temperature coefficients of the molecular conductivity are positive in the most concentrated and in the most dilute solutions, but negative in the intermediate solutions. Similar anomalous behaviour has been observed by Franklin (*J. Physical Chem.*, 1911, **15**, 675) for solutions of potassium iodide in liquid sulphur dioxide.

Any complex molecular and ionic species in solution will tend to break up both with rising temperature and with increasing dilution. It seems, therefore, that in order to explain the anomalous changes in the temperature coefficient, it is necessary to assume the existence of *at least three* molecular (or complex ionic) species in solution, the intermediate one having the largest conductivity, owing either to its more extensive dissociation or to the greater mobility of its ions.

The molecular conductivity of the most dilute solution (*V* = 8069) at 25° is only 49·98, whilst the ionic conductivity of the iodine ion is 96 (Walden, "Elektrochemie nichtwässeriger Lösungen," p. 186), so that the cadmium iodide cannot be regarded as completely dissociated even at a dilution of 8000 litres. It should be noted that the temperature coefficients of the molecular conductivity tend (for the last three solutions) with increasing dilution towards the value of the temperature coefficient of the fluidity of acetonitrile, *viz.*, 0·0113.

In conclusion, the author gladly takes this opportunity of expressing his thanks to Professor J. C. Philip, F.R.S., for his constant interest and advice.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, January 26th,* 1927.]

XCIX.—*On the Alleged Retardation of Certain Reactions by Light.*

By ARTHUR JOHN ALLMAND and ROBERT EDWIN WITTON MADDISON.

ABOUT twenty years ago, Trautz published some papers (*Physikal. Z.*, 1906, 7, 899; *Z. wiss. Phot.*, 1906, 4, 351; *Z. Elektrochem.*, 1907, **13**, 550) in which he discussed the possibility of the retardation of chemical reactions by light, supporting his deductions by a series of experimental observations. The dissertation published later by Thomas (Freiburg i. B., 1908) contains further details with regard to the latter. In all cases but one (the decomposition of hydrogen peroxide), the reactions studied were those between oxygen and an aqueous solution of some oxidisable substance. A manometric method was usually employed, solution and oxygen standing in contact with one another inside a vessel similar to a gas pipette, which was closed by a U-shaped manometer open on one side to the air. Several such pipettes were used simultaneously, each being enclosed in a glass sheath containing a certain filter solution, except that the pipette serving for the dark control experiment was contained in a galvanised-iron sheath filled with water. The whole set of pipettes with their sheaths was placed in a large vessel filled with water which stood near a window. The water was stirred from time to time and it was assumed that comparable temperature conditions were obtained, although, as the experiments in some cases extended over several days and nights, this appears doubtful. In any case, the results are said to have been reproducible. In some experiments (notably those with sodium sulphide solutions and red light), a shaking apparatus in a thermostat was employed.

The following remarkable results were claimed. Violet light retards the reaction of oxygen with aqueous solutions of sodium sulphide, of sodium sulphite, and of pyrogallol, and with cuprous chloride dissolved in ammonia or in hydrochloric acid. Red light retards the decomposition of aqueous hydrogen peroxide, and the oxidation of cuprous chloride in hydrochloric acid, of aqueous pyrogallol, and of benzaldehyde. Below 23°, it also retards the oxidation of sodium sulphide, but above 25° it accelerates it. Green light retards the oxidation of solutions of cuprous chloride in ammonia, whilst both green and yellow light retard the oxidation of aqueous sodium sulphite. Almost equally striking results are reported with regard to the accelerating effects of light of different colours on the same reactions.

To explain these results, Trautz suggests that the observed velocity in the dark must be regarded as compounded of two opposed velocities, forward and back, and that these opposed reactions are affected in different degrees by light. If the reverse reaction is accelerated to a greater extent than the forward reaction, a net retardation will result on illumination. This view involves the consequence that the thermal (dark) equilibrium ultimately reached in the reaction concerned must be displaced by light. No evidence that this is so is brought forward, nor do the known facts of photochemistry suggest that such a displacement occurs frequently. Trautz leaves it open as to whether the reaction obeys the same laws of kinetics in the light as in the dark, with mere alteration of coefficients, or whether the total reaction in light is to be regarded as made up of separate light and dark reactions, superposed additively on one another.

Several reasons led us to carry out experiments on this subject. They were (1) the remarkable nature of the effects claimed, even when "colourless" solutions, with negligible absorption in the visible region, were employed; (2) the lack of confirmatory data on equilibrium displacement in light (not merely in these experiments, where the detection of the displacement might well be difficult, but in photochemical reactions generally); (3) the probability that, in some reactions at all events, *diffusion* rates were in reality being measured; (4) the facts that the detailed figures given by Thomas, are, in general, irregular when plotted, and that, in the experiments on the oxidation of sodium sulphide solutions, "retardation" by violet light was observed to have taken place *during the night hours* almost as frequently as during the day, whilst on several occasions "acceleration," not "retardation," was noted during the day hours (points which only become apparent when the data for an experiment lasting over several days are considered in detail); (5) the absence of any indication that the use of a particular pipette did not in some way lead to specific results; (6) the fact that the degree of temperature control obtained did not seem adequate when the manometric method of following the rate of reaction is considered.

EXPERIMENTAL.

The majority of our experiments were carried out on the oxidation of sodium sulphite solutions, where the high transparency in the visible region, maintained during the whole reaction, ensures a uniform light field throughout the solution from start to finish. Instead of allowing the oxygen to diffuse into the solution, as did Thomas, we passed a brisk current of air through continuously, and any likelihood of a diffusion reaction being measured was thus eliminated. The type of reaction vessel used (a cell composed of quartz plates cemented on to the ends of a 7·5 cm.-diameter circular cavity drilled through a glass block) has been described elsewhere (J., 1925, **127**, 829). In the present case, the glass block was 5 cm. in thickness. Two holes bored through its upper surface into the central cavity served for the introduction of a thermometer and of the pipette for abstracting samples of liquid for analysis, whilst a similar hole passing through the side of the block into the interior of the cell at its lowest level had cemented into it a glass tube for leading in the air-stream. In front of this vessel was placed a combined water-cooling and filter cell of similar construction (four quartz plates alternating with three glass frames of thickness 1·0, 0·5 and 0·5 cm., respectively, the whole cemented together). Through the compartment of this cell nearest the light source (1 cm. in depth), a current of tap-water was kept continuously flowing, whilst the other compartments (0·5 cm. in depth) contained the filter solutions (or distilled water in other cases). The whole was placed in a wooden box, blackened inside, covered with tin foil outside, and furnished with sliding shutters on each of two opposite sides, for entry of the light beam and, when required, for inspection. Holes in the lid were provided for the air-supply tube, the thermometer, and the pipette, and also for an additional thermometer used to register the temperature in the box itself (outside the reaction cell). The air stream was produced by a motor-driven positive blower, and passed through a tube packed with activated charcoal, a simple calibrated differential flow-meter, and a wash-bottle filled with some of the sodium sulphite solution, before entering the reaction vessel. A steady rate of supply was maintained by regulating a resistance in the motor circuit, and by adjusting a screw-clip on a rubber connexion between the blower and the flow-meter. 150 C.c. of solution were generally employed.

The analysis was carried out by removing 5 or 10 c.c. in a pipette, running them into 20 c.c. of 0·1*N*-iodine, acidified with dilute hydrochloric acid, and titrating back with 0·1*N*-sodium thiosulphate.

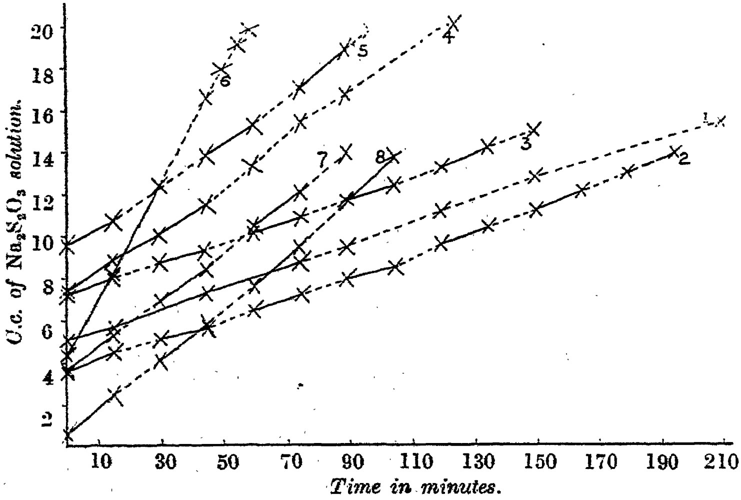
For most of the experiments, the light source was a quartz mercury lamp, placed 13 cm. away from the front of the reaction cell. For red light, a 500-watt Osram lamp was employed at a distance of 18 inches, and an additional glass water-cooler was placed outside the box in the path of the beam. The temperature generally rose about 2° during a complete experiment. The thermometer in the box outside the cell was, of course, chiefly affected during the "light" period, but the temperature of the solution inside the cell rose more or less uniformly during both light and dark periods. In any case the results show that any temperature effect was negligible. The filter solutions used are given in the following table. They were far from being monochromatic but, in view of the nature of the experiments, no particular importance was attached to this.

Nature of light.	Filter.
Short ultra-violet (below 265 $\mu\mu$—also visible light).	(*a*) 0·5 cm. $N/1600$-*p*-nitrophenol. (*b*) 0·5 cm. 0·002% *p*-nitrosodimethylaniline.
Long ultra-violet (365 $\mu\mu$—also some blue and violet).	0·5 cm. 0·0625% acid fuchsine.
Blue-violet (405—436 $\mu\mu$).	(*a*) 0·5 cm. 0·0125% acid fuchsine. (*b*) 0·5 cm. 0·2% quinine sulphate.
Green (500—550 $\mu\mu$).	1 cm. of an alcoholic solution of 2·4% $CoCl_2$ + 2·4% $NiCl_2$ + 0·1% fluorescein (similar to that used by Thomas).
Red (also small amounts of blue and violet).	(*a*) 0·5 cm. 10% ferrous ammonium sulphate. (*b*) 0·5 cm. 0·075% acid fuchsine.

Originally, alternate dark and light experiments, using different fillings in the cell each time, were carried out. The results were very discordant, successive runs on different portions of the same solution sometimes indicating an acceleration in light and sometimes a retardation. The difficulty of accurate control of the rate of dark oxidation of sodium sulphite solutions is well known and has recently been discussed by Rice from a new point of view (*J. Amer. Chem. Soc.*, 1926, **48**, 2099). We therefore altered our procedure and, without removing the solution from the cell, observed its rate of oxidation during successive dark and light periods, removing samples for analysis at the end of each of such periods. Under these conditions, the rate of dark oxidation remained reasonably constant when a particular cell filling was used. The variations in the slopes of the curves for different cell fillings show plainly the impossibility of obtaining conclusive results by the first method. Our data are shown in the figure, where c.c. of 0·1N-sodium thiosulphate are plotted against time. Dark periods are shown by continuous, light periods by broken lines. Violet light was used in Expts. 1 and 2, red light in 7 and 8, green in 6, ultra-violet light of long wave-length in 3, and short wave-length ultra-violet light in 4 and 5. In plotting the results of 7 and 8, in order to separate the curves better, 4 c.c. have been subtracted throughout from the actual numbers used in the titrations.

In addition, a few experiments using red light were carried out with an apparatus similar to that of Thomas, the chief changes being that a straight mercury manometer was used, instead of the U-tube type employed by him, and, in addition, that the pipettes were immersed in a thermostat at 25°. The solutions used were aqueous sodium sulphite and ammoniacal cuprous chloride—in both cases red light is said to accelerate the oxidation. Two pipettes were employed and the method of alternate light and dark periods was used. There is no need to give the results in detail. When manometer readings were plotted against time, regular curves were obtained with nothing whatever to indicate any accelerating effect of the red light.

FIG. 1.



Discussion and Conclusions.

It will be seen that, within the limits of experimental error, none of our results indicates any effect of light on the rate of oxidation of aqueous sodium sulphite with the exception of Expt. 4 and (more doubtfully) Expt. 5. In those cases, ultra-violet light of short wave-length was being used, and the work of Mathews and his collaborators (*J. Physical Chem.*, 1913, **17**, 211; 1926, **30**, 414; *J. Amer. Chem. Soc.*, 1917, **39**, 635) has already shown that such light, which falls within the strong ultra-violet absorption band of sodium sulphite, accelerates its oxidation (compare the case of sodium bisulphite or metabisulphite—Baly and Bailey, J., 1922, **121**, 1813; Dietzel and Galanos, *Z. Elektrochem.*, 1925, **31**, 466; Getman, *J. Physical Chem.*, 1926, **30**, 266), This being the case, and taking into account the criticisms of the work of Trautz and Thomas made above, we are of opinion that the effects they observed were due, not to light, but rather to incomplete control of the dark reaction (such as would result from variable diffusion rates or variable amounts of positive catalysts associated with a particular filling or a particular pipette), and that, consequently, their results are probably spurious and cannot be regarded as evidence in favour of the possibility of photochemical retardation.

The above experiments were carried out during 1923. The junior author wishes to acknowledge his indebtedness to the Scientific and Industrial Research Department for a maintenance grant which enabled him to take part in the work.

UNIVERSITY OF LONDON,
KING'S COLLEGE.
[*Received, January 14th*, 1927.]

C.—*The Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. Part II.*

By ARTHUR JOHN ALLMAND, PERCY WALMSLEY CUNLIFFE, and ROBERT EDWIN WITTON MADDISON.

IN Part I of this investigation (J., 1925, **127**, 822), we recorded our work on the factors affecting the proportions of the reaction products—oxygen and chloric acid. The present paper contains our results on the energetics of the reaction, and a suggested theory of the whole.

EXPERIMENTAL.

Extinction Coefficients.—These were determined by means of an ultra-violet spectrometer (Hilger), thermopile (Hilger), and galvanometer (Paschen), a quartz–mercury lamp being used as light source. The absorption cells were of the type already described (*loc. cit.*, p. 829), with crystal quartz ends. Two similar ones were employed, after being tested, when filled with distilled water, for equality of transmission over the wave-length range used.

One contained the solution under examination, the other distilled water; the ratio of the galvanometer deflexions therefore gave the fractional transmission of the solution. Cells of 5 and 0·5 cm. depth were used. No extraordinary accuracy is claimed for the results, in consequence of the difficulty experienced at that time in obtaining steady deflexions with the Paschen galvanometer at high sensitivity. Only those figures used in the subsequent calculations and discussion are therefore given. When values differed appreciably amongst themselves, those obtained from solutions with very low transmissions have been omitted. The units used are the mol., litre, and cm., together with Briggsian logarithms. The figures in the last two lines of the table we owe to Mr. H. J. Taylor.

TABLE I.

	Molecular extinction coefficient (k).		
Solution.	365 $\mu\mu$.	405 $\mu\mu$.	436 $\mu\mu$.
0·0145M-Cl_2	9·25	—	0·56
0·0375M-Cl_2	14·7	2·12	0·64
0·043M-Cl_2	—	2·43	0·74
0·0645M-Cl_2 + 0·01N-HCl	—	2·99	0·96
0·0115M-Cl_2 + 0·5N-HCl	—	7·51	2·7
0·045M-Cl_2 + 0·5N-HCl	—	3·85	1·38
0·051M-Cl_2 + 0·01N-KCl	—	2·9	1·16
0·045M-Cl_2 + 0·5N-KCl	—	5·1	2·1
0·0495M-Cl_2 + 0·01N-H_2SO_4	—	2·6	0·84
0·045M-Cl_2 + 0·5N-H_2SO_4	—	3·4	1·2
0·054M-Cl_2 + 0·01N-Na_2SO_4	—	2·3	0·74
0·047M-Cl_2 + 0·5N-Na_2SO_4	—	2·0	0·75 ?
0·049M-Cl_2 + Sat. Na_2SO_4	5·6	1·16	0·46
0·049—0·9M-HClO	1·2	0·19	0·13
0·045M-HClO + 0·5M-Na_2HPO_4	5	0·61	0·22 ?
0·024M-HClO + 0·125M-Na_2HPO_4	4·16	0·60	0·40
0·040M-HClO + 0·125M-Na_2HPO_4	3·59	0·43	0·37

In addition, k_{313} for 0·49—0·9M-HClO and for 0·0375M-Cl_2 were found to be respectively 18·2 and about 47.

Certain points in the table call for comment. In chlorine water, free from any addition, the values of k increase with concentration. The addition of hydrochloric acid increases k, and the more so the greater the ratio [HCl]/[Cl_2]. On the other hand, addition of sodium sulphate decreases the extinction. The last two effects are both visible to the eye. In all solutions containing chlorine, k_{405}/k_{436} is near 3. Solutions of hypochlorous acid have smaller k values than those containing chlorine, and k_{405} and k_{436} are nearer one another. The addition of disodium hydrogen phosphate increases the extinction. In all solutions examined, whether of chlorine or hypochlorous acid, the ratio k_{365}/k_{405} is of the order 5—9. We regard the effect on k of the addition of sodium phosphate to hypochlorous acid as independent evidence that, in such solutions, the reaction $HClO + HPO_4'' \longrightarrow H_2PO_4' + ClO'$

takes place to an appreciable extent (*loc. cit.*, p. 825). The increase in the extinction with increasing ratio $[Na_2HPO_4]/[HClO]$ would indicate k values for the hypochlorite ion greater than those for hypochlorous acid, and preliminary measurements indicate that k_{365} for this ion is about 9. The rise in extinction for chlorine solutions with increasing concentration is readily explicable by the changing degree of hydrolysis, the k values for chlorine being greater than those of hypochlorous acid. Assuming $K = [H^{\cdot}][Cl'][HClO]/[Cl_2]$ to be $3{\cdot}8 \times 10^{-4}$ for our solutions (value interpolated from table on p. 508 of Lewis and Randall's "Thermodynamics"), we calculate the concentrations in the chlorine-water solutions given at the head of our table to be as follows:

(*a*) $0{\cdot}0035M$-Cl_2 + $0{\cdot}011M$-$HClO$ (total $0{\cdot}0145M$).
(*b*) $0{\cdot}0185M$-Cl_2 + $0{\cdot}019M$-$HClO$ (total $0{\cdot}0375M$).
(*c*) $0{\cdot}023M$-Cl_2 + $0{\cdot}02M$-$HClO$ (total $0{\cdot}043M$).

Combining these data by means of the equation $\log I_0/I = d(C_{HClO} \cdot k_{HClO} + C_{Cl_2} \cdot k_{Cl_2})$, where d = the depth of the solution, with the measured transmissions of the solutions and the k_{HClO} values given above, we have calculated the values for k_{Cl_2} given in the second column of Table II. The remaining columns contain k values calculated for chlorine gas from (i) the accurate work of von Halban and Siedentopf (*Z. physikal. Chem.*, 1922, **103**, 71); (ii) some rough measurements made by one of us (P. W. C.) in conjunction with Dr. Reeve; (iii) more recent data obtained in this laboratory. The general nature of the agreement between the figures for dissolved and gaseous chlorine is of distinct interest.

TABLE II.

	k_{Cl_2}.			
		For gas.		
Wave-length.	In chlorine water.	(v. H. and S.).	(C. and R.).	(recent figs.).
$313\mu\mu$	(77)	53	33·6	—
365	34; 29	27	20·6	24·7
405	4·4; 4·1; 3·2	4	4·6	4·4
436	0·96; 1·29; 1·94	2	3·7	1·9

Measurements of Quantum Efficiency.—A number of experiments were carried out, using one or another of several quartz–mercury lamps arranged to give "parallel" beams of known energy distribution and total energy flux, and filters intended to pass monochromatic radiation of wave-length $365\ \mu\mu$.

The energy absorbed in the reaction cell was computed by means of the extinction coefficients given above, and the quantum efficiency calculated from the degree of decomposition. The exact experimental procedure used was varied during the course of the work, but in outline the method was as follows. The mercury lamp was situated immediately behind a metal screen in which was cut a circular aperture of 1—2 cm. diameter. This diaphragm was placed at the focus of a quartz lens (diameter, 8 cm.; focal length, 10—11 cm.), and the resultant approximately parallel beam passed through a water cell (for absorbing heat rays) and a cell containing the filter solution, before falling on the reaction vessel. The cells used were all of the type already described (*loc. cit.*, p. 829), their ends consisting of crystal quartz plates. The reaction vessel was 5 cm. deep in every case. Any chlorine carried forward by the evolved oxygen was, as before, trapped in a potassium iodide solution, and the necessary correction applied.

The intensities of the beams used were by no means uniform over their whole cross-section. In order to obtain the total incident energy flux on the surface of the reaction vessel, the filter cell was filled with distilled water, and the thermopile–galvanometer deflexion read with the thermopile placed in a number of representative positions in the path of the beam, and in the plane which was later occupied during the actual measurements by the front of the reaction vessel. The thermopile–galvanometer combination (in some experiments a Coblentz pile and Broca galvanometer, in others a Moll pile and Gambrell galvanometer) had previously been calibrated by means of a standard Hefner lamp. The average *H.K.* intensity of the unfiltered beam was thus obtained, and this, when combined with its measured energy-distribution, determined as described elsewhere (*J. Physical Chem.*, 1925, **29**, 713), with the spectral transmission of the filter used, with the insolated area of the solution under investigation, and corrected for reflexion at the front surface of the reaction cell, made it possible to calculate completely the intensity and the nature of the radiant energy flux entering the solution. The extinction coefficients of the different solutions were estimated for the beginning and end of the reaction by interpolation between the experimental figures already given, taking account of the change due to the production of hydrogen chloride by insolation. From these figures the initial and final absorptions were deduced, and the arithmetic mean was taken for the calculation of γ. In the case of chlorine in lithium chloride, no exact data were available, but both the appearance and photographs taken with a Judd Lewis photometer and quartz spectrograph indicated very high absorption.

Under the above experimental conditions, the lamps used gave beams of the following intensity and energy distribution.

TABLE III.

Lamp No.	Total intensity.	Fraction of total intensity.			
		313 $\mu\mu$.	365 $\mu\mu$.	405 $\mu\mu$.	436 $\mu\mu$.
1	25·9 *H.K.*	0·086	0·188	0·070	0·129
2	27·87	0·069	0·180	0·078	0·151
3	39·72	0·078	0·190	0·068	0·152

The filter employed for Expt. 1, Table V, consisted of 1 cm. of 0·03125% Diamond Fuchsine (Cassella). In Expts. 2 and 3, 5 mm. of 0·0625% Acid Fuchsine (B. D. H.) were used, and in Expts. 4—8, 5 mm. of a 0·075% solution of the same substance. This change from the Cassella to the B. D. H. dyestuff proved to be unfortunate, as subsequent measurements showed the latter to absorb diffusely, and to pass high proportions of the violet and blue lines. Although this unfavourable circumstance is partly corrected by the higher proportion of the 365 $\mu\mu$ component in the unfiltered beam, and by its greater absorption in the solutions used, the result is that the γ values obtained in these experiments are only average figures, corresponding to a mean wavelength which lies between 365—405 $\mu\mu$ and varies from experiment to experiment. The transmissions of the actual solutions (determined by the Hilger thermopile and Paschen galvanometer) are given in Table IV.

TABLE IV.

Expt.	Filter.	Fractional transmission of			
		313 $\mu\mu$.	365 $\mu\mu$.	405 $\mu\mu$.	436 $\mu\mu$.
1	1 cm. 0·03125% Diamond Fuchsine.	0·013	0·365	0·013	Nil.
2, 3	0·5 cm. 0·0625% Acid Fuchsine.	Nil.	0·234	0·333	0·115
4—8	0·5 cm. 0·075% Acid Fuchsine.	Nil.	0·175	0·267	0·075

The calculation is given in full for the simplest case only (Expt. 1) where the small amounts of absorbed energy belonging to lines other than 365 $\mu\mu$ were neglected (error involved about 2%).

Lamp used : No. 1. Fraction of 365 $\mu\mu$ energy absorbed : 1·0. Duration of expt. : 41·5 hours. Average surface of insolated solution : 31·6 cm.^{2}.
Energy in unfiltered beam incident on cell $= a =$ 25·9 *H.K.*
Ergs in unfiltered beam incident on cell $= a = 25{\cdot}9 \times 945$/cm.^{2}/sec.
Ergs of 365 $\mu\mu$ in unfiltered beam incident on cell $= b = a \times 0{\cdot}188$/cm.^{2}/sec.
Ergs of 365 $\mu\mu$ in filtered beam incident on cell $= c = b \times 0{\cdot}365$/cm.^{2}/sec.
Ergs of 365 $\mu\mu$ in filtered beam incident on solution $= d = c \times 0{\cdot}95$/cm.^{2}/sec.
Ergs of 365 $\mu\mu$ in filtered beam incident on solution $= e = d \times 31{\cdot}6$/sec.
Ergs of 365 $\mu\mu$ incident on and absorbed by solution in course of run $= f = e \times 41{\cdot}5 \times 3600$.
Quanta of 365 $\mu\mu$ incident on and absorbed by solution in course of run $= g = f \div (6{\cdot}57 \times 822 \times 10^{-15})$.
$= 1{\cdot}40 \times 10^{21}$.
Molecules of chlorine decomposed in course of run $= 0{\cdot}00366 \times 6{\cdot}06 \times 10^{23}$.
$= 2{\cdot}22 \times 10^{21}$.

Hence $\gamma = 2{\cdot}22/1{\cdot}40 = 1{\cdot}59$.

TABLE V.

No. of expt.	Lamp. used.	Solution.	Initial conc. of Cl_2(HClO). *M*.	Duration of insolation (hrs.).	Loss in titre by decomposition. *M*.	$HClO_3$ yield (%).	Initial fraction of incident energy absorbed. 365 μμ.	Initial fraction 405 μμ.	Initial fraction 436 μμ.	Final fraction of incident energy absorbed. 365 μμ.	Final fraction 405 μμ.	Final fraction 436 μμ.	Absorbed quanta (× 10^{-20}). 365 μμ.	Absorbed quanta 405 μμ.	Absorbed quanta 436 μμ.	Molecules decomposed (× 10^{-20}).	γ.
1	1	Cl_2 water.	0·0503	41·5	0·02305	46	1·0	—	—	As at start.			14·0	—	—	22·2	1·59
2	2	,,	0·02725	23·0	0·01515	62	0·977	0·466	0·172	0·984	0·499	0·198	7·01	2·37	0·65	20·35	2·03
3	2	,,	0·0550	30·0	0·02535	61	1·0	0·807	0·386	1·0	0·808	0·411	9·33	5·18	1·84	34·0	2·08
4	3	Cl_2 water +0·004*N*-HCl.	0·0405	27·0	0·0052	56	1·0	0·741	0·373	1·0	0·749	0·386	9·48	4·30	1·54	6·96	0·45
5	3	Cl_2 water +0·6*N*-HCl.	0·03775	48·25	0·0012	—	1·0	0·88	0·535	As at start.			16·93	9·07	3·87	1·61	0·054
6	3	Cl_2 water +0·5*N*-LiCl.	0·0440	46	0·00615	39	1·0	1·0	1·0	As at start.			16·15	9·83	6·90	8·24	0·25
7	3	Cl_2 water +0·33*M*-Na_2SO_4.	0·0330	26·75	0·0040	—	0·967	0·495	0·204	As at start.			9·08	4·30	1·54	5·36	0·42
8	3	HClO +0·125*M*-Na_2HPO_4.	0·05575	69	0·0300	86	0·872	0·226	0·204	0·695	0·156	0·112	19·0	2·8	1·6	40·2	1·72

Table V contains the results of our measurements, for which the accuracy claimed does not exceed 10—15%.

It will be noticed that γ for decomposition of chlorine water is much lowered by the addition either of hydrochloric acid or of the two neutral salts tested, results predicted by the observations of Bunsen and Roscoe (*Pogg. Ann.*, 1855, **96**, 373), Milbauer (*Z. physikal. Chem.*, 1914, **86**, 564), Benrath and Schaffganz (*ibid.*, 1922, **103**, 139), and others. The effect of the very small initial addition of hydrochloric acid in Expt. 4 is striking, and probably connected with the decreased yield of chloric acid remarked on in Part I of this work. Whilst, however, the addition of a chloride, besides lowering γ, decreases the yield of chloric acid and increases both extinction and the partial pressure of chlorine above the liquid, in the case of sodium sulphate the decreased quantum efficiency is accompanied by a decreased extinction and lowered partial pressure of chlorine, whilst the yield of chloric acid is practically unaffected (Part I, p. 834). Hypochlorous acid is seen to be, at all events, not more photosensitive than chlorine water under the conditions prevailing, whereas the reverse behaviour was originally anticipated (Part I, pp. 823, 824). It will be noted that γ in Expt. 1 is considerably lower than in Expts. 2 and 3. We think this may be connected with the low percentage of chloric acid found in the products, considerably the lowest of any ever obtained by us with chlorine water, and confirmed by several titrations during the course of the experiment. Qualitatively, it would suggest the presence of hydrochloric acid in the original chlorine water, perhaps due to insufficient washing of the gas.

Quantum Efficiency and Wave-Length.—Three experiments were carried out in which chlorine water was exposed under comparable conditions to monochromatic light of wave-lengths 313 $\mu\mu$, 365 $\mu\mu$, and 436 $\mu\mu$, of known relative, but not absolute, intensity. The filters employed were, respectively:

(*a*) 5 mm. of 0·0125% Diamond Fuchsine + 5 mm. of 0·0125% Auramine O.

(*b*) 1 cm. of 0·03125% Diamond Fuchsine.

(*c*) 5 mm. of 0·0857% Victoria Blue + 5 mm. of 4% quinine sulphate.

The results are in Table VI.

The figures stand in the usual order of increasing γ with increasing frequency, but we lay no stress on this, in view of the probable experimental error. The results might equally well be interpreted as indicating that γ is independent of λ.

TABLE VI.

Wave-length.	Relative incident intensity.	Average fraction absorbed.	Relative absorption rate (watts).	Initial titre. (M).	Loss in titre during 30 hrs.	Relative quanta absorbed.	Relative γ ($\gamma_{365}=1$).
313 $\mu\mu$	2·0	1·0	2·0	0·0445	0·0074	2·09	1·02
365	6·36	1·0	6·36	0·0515	0·0268	7·75	1·00
436	8·40	0·366	3·07	0·0497	0·0130	4·46	0·84

Discussion.

Any proposed reaction mechanism must account for the experimental facts described in this and in the preceding paper, of which the following are the most important.

(i) The yields of chloric acid during the photolysis of hypochlorous acid and of chlorine water are nearly the same; they are considerably increased by adding sodium phosphate, less so by lithium sulphate, slightly raised by sodium sulphate, and slightly diminished by sulphuric acid; they are depressed by adding strongly dissociated chlorides, which are effective in the order HCl>KCl>LiCl.

(ii) The same chlorides increase the extinction coefficients of chlorine water, the order of effectiveness now being LiCl>KCl>HCl. At the same time the partial pressure of the chlorine rises, as shown by the amounts volatilised during the insolations.

(iii) Lithium and sodium sulphates decrease both volatility of chlorine and extinction coefficient; the addition of sulphuric acid hardly affects the former, whilst slightly increasing k.

(iv) The three electrolytes so far tested (hydrogen chloride, lithium chloride, and sodium sulphate) all decrease γ_{365} for decomposition of chlorine water, the first being by far the most effective in this respect. γ_{365} for the photolysis of a hypochlorous acid solution containing sodium phosphate is lower than that for chlorine water.

(v) The actual value of γ_{365} for pure chlorine water under the conditions of experiment is about 2, and it varies but little with frequency between the limits 313—436 $\mu\mu$.

(vi) There is obviously a close similarity between the two photolyses.

Many possible reaction mechanisms have been considered and dismissed as involving unlikely assumptions or as leading to conclusions inconsistent with the experimental results. Thus, for hypochlorous acid photolysis, combinations of the following were considered.

	Mechanism.	γ.	Yield of chloric acid (%).
(a)	$\left\{\begin{array}{l} HClO + h\nu \longrightarrow HCl + O, \\ HClO + O \longrightarrow HClO_2, \\ HClO_2 + HClO \longrightarrow HClO_3 + HCl. \end{array}\right.$	3	100
(b)	$\left\{\begin{array}{l} 2HClO + 2h\nu \longrightarrow 2HCl + 2O, \\ 2O \longrightarrow O_2', \\ O_2' + HClO \longrightarrow HClO_3. \end{array}\right.$	1·5	100
(c)	$\left\{\begin{array}{l} 2HClO + 2h\nu \longrightarrow HCl + 2O, \\ O + HClO \longrightarrow HClO_2, \\ O + HClO_2 \longrightarrow HClO_3. \end{array}\right.$	1·5	100
(d)	$\left\{\begin{array}{l} 2HClO + 2h\nu \longrightarrow 2HCl + 2O, \\ 2HClO + 2O \longrightarrow 2HClO_2, \\ 2HClO_2 \longrightarrow HClO_3 + HClO. \end{array}\right.$	1·5	100
(e)	$\left\{\begin{array}{l} HClO + h\nu \longrightarrow HCl + O, \\ O + HClO \longrightarrow HCl + O_2. \end{array}\right.$	2	0
(f)	$\left\{\begin{array}{l} 2HClO + 2h\nu \longrightarrow 2HCl + 2O, \\ 2O \longrightarrow O_2. \end{array}\right.$	1	0

Similar schemes were considered for chlorine water, in which $Cl_2 + H_2O$ took the place of HClO, as also mechanisms involving as primary reactions dissociation of the chlorine molecule, either directly or after collision between an activated and a normal molecule.

We have finally been led to suggest the following reaction mechanisms.

	For hypochlorous acid.	For chlorine water.
A	$HClO + h\nu \longrightarrow HCl + O,$	$Cl_2,H_2O + h\nu \longrightarrow 2HCl + O,$
{ *B*	$\tfrac{1}{2}(2O \longrightarrow O_2'),$	$\tfrac{1}{2}(2O \longrightarrow O_2'),$
{ *or C*	$HClO + O \longrightarrow HCl + O_2',$	$Cl_2,H_2O + O \longrightarrow 2HCl + O_2',$
{ *D*	$HClO + O_2' \longrightarrow HClO_3,$	$Cl_2,H_2O + O_2' \longrightarrow HClO_3 + HCl,$
{ *or E*	$O_2' \longrightarrow O_2.$	$O_2' \longrightarrow O_2.$

By Cl_2,H_2O is meant, not necessarily a molecule of a " chemical " chlorine hydrate, but rather a grouping of molecules of these two substances in sufficiently close association to render possible the reactions ascribed to it.

The maximum attainable value of γ (processes *A*, *C*, *D*) will be 3, with a 100% yield of chloric acid. Processes *A*, *B*, *E* [(f) above] will result in $\gamma = 1$ and $HClO_3 = 0\%$; processes *A*, *B*, *D* [(b) above] in $\gamma = 1{\cdot}5$ and $HClO_3 = 100\%$; and processes *A*, *C*, *E* [(e) above] in $\gamma = 2$ and $HClO_3 = 0\%$. Let a be the fraction of absorbed quanta resulting in the process *A*, b and c the fractions of the total oxygen atoms produced by *A* reacting in accordance with *B* and *C*, respectively ($b + c = 1$), and d and e the fractions of activated O_2' molecules reacting in *D* and *E*, respectively ($d + e = 1$). Then it is clear that the observed quantum efficiency will be higher the greater a, c/b, and d/e, whilst the chloric acid yield will depend solely on d/e. The proposed mechanism thus allows of a very low γ value accompanying a 100% yield of chloric acid, but, on the other hand, excludes the possibility of γ exceeding 2 unless chloric acid is produced. It also brings out clearly the essential similarity between the hypochlorous acid and chlorine-water photolyses.

Further consideration of these reaction stages suggests the probability that b is negligible compared with c, except in very dilute solutions (see later). We therefore put $b = 0$, $c = 1$, for purposes of calculation, and thus arrive at the simple relations

$$\gamma = 2a + ad = a(2 + d)$$

$$\mathrm{HClO_3}\text{ yield }(\%) = 100 \times 3ad/(2a + ad) = 100 \times 3d/(2 + d)$$

which, given γ and the chloric acid yield, allow us to calculate both a and d—or d alone, if only the chloric acid yield is available. Table VII contains, for the experiments of Table V, the values of a and d, whilst Table VIII contains d values for different solutions, calculated from the chloric acid yields given in Part I.

TABLE VII.

Expt.	1.	2.	3.	4.	5.	6.	7.	8.
a	0·67	0·80	0·83	0·18	0·026	0·11	0·17	0·61
d	0·37	0·53	0·52	0·47	0·1	0·3	0·53	0·81

TABLE VIII.

Solution.	HClO.	HClO + M/8-Na_2HPO_4.	HClO + M/4-Na_2HPO_4.	Cl_2 water.	Cl_2 water + 2N-Li_2SO_4.
d.	0·52	0·81	0·73	0·52	0·65

Solution.	Cl_2 water + N/4-Li_2SO_4.	Cl_2 water + Na_2SO_4.	Cl_2 water + N/10-H_2SO_4.	Cl_2 water + N/2-H_2SO_4.	Cl_2 water + N/10-KCl.
d.	0·54	0·53	0·5	0·47	0·51

Solution.	Cl_2 water + N/2-KCl.	Cl_2 water + N/2-LiCl.	Cl_2 water + N/250-HCl.	Cl_2 water + N/100-HCl.	Cl_2 water + N/10-HCl.	Cl_2 water + N/2-HCl.
d.	0·22	0·3	0·47	0·46	0·22	0·1

The d *Coefficients.*—These express the fraction of O_2' molecules which collide with HClO molecules or Cl_2,H_2O groupings and thereby produce a molecule of chloric acid; $1 - d$ represents the fraction of such molecules which either undergo such a collision without result, or else become deactivated before collision. Clearly, if this mechanism holds good, the chloric acid yield would be expected eventually to diminish with fall of concentration, unless some kind of a compensating influence were active; and the shorter the average life of the activated molecule, the higher the concentration at which this effect would be anticipated. No definite sign of this falling off has so far been found in our experiments (*loc. cit.*, p. 833), which may indicate that the life of the O_2' molecule under the conditions prevailing was, in general, long enough to ensure a normally effective collision before deactivation. In dilute solutions of chlorine water, however, a compensating influence of the kind mentioned may be active, *viz.*, an increased proportion of hypochlorous acid molecules resulting from greater hydrolysis, for the high *d* values with solutions of hypochlorous acid containing sodium phosphate suggest that hypochlorous acid molecules are better acceptors for O_2' molecules than are the Cl_2,H_2O groupings under the experimental conditions. Indeed, the difference is probably greater than appears from the above figures, for, as has been seen, there is reason to suppose that a proportion of hypochlorite ions, increasing with concentration of sodium phosphate, is present in these solutions, and other measurements point to their being comparatively bad acceptors for O_2' molecules.

The effect of *sulphates* is interesting, and can be considered in conjunction with the concomitant changes in the degree of volatility of the chlorine and in the extinction. We suggest that addition of sulphuric acid slightly increases the free chlorine concentration (when added in small amounts, at all events, in accordance with the Jakowkin equilibrium). The observed results are consistent with this view and with our hypothesis on the relative efficiencies of the acceptors HClO and Cl_2,H_2O. In the case of lithium and sodium sulphates, we assume the reaction $H^{\bullet} + SO_4'' \longrightarrow HSO_4'$ to take place, a change probably responsible for the results of Thomas and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41**, 1981) on the effect of the addition of sulphates on the hydrogen-ion concentration (activity) in 0·1*N*-hydrochloric acid. This would cause the displacement of the Jakowkin equilibrium in the direction of increasing chlorine hydrolysis and a greater hypochlorous acid concentration; this, in turn, would account for the changes in volatility of chlorine, extinction, and yield of chloric acid.

The influence of *chlorides* is more complex. From a consideration of the data, it would appear to be two-fold—a lowering of the *d* coefficients due to the chlorine ion, and an opposed effect, depending on the kation, running parallel with an increase in extinction and volatility (*i.e.*, chlorine activity), and increasing as we pass from hydrochloric acid through potassium chloride to lithium chloride (order of increasing "hydration"). More will not be suggested at this stage, as we think that our results with chlorine water in chloride solutions need further elucidation and confirmation from several points of view. In addition, the formation of chlorine ions during insolation is a complicating factor.

The a *Coefficients.*—Those for chlorine water without any addition (Expts. 1—3) are seen to exceed that for hypochlorous acid in sodium phosphate solution (Expt. 8). In view of the fact that hydrochloric acid, which lowers these coefficients very considerably, is produced during the reaction, it does not seem unreasonable to imagine that, if the effect due to this acid could be eliminated, a might be unity. It has already been mentioned that the nature of the results in Expt. 1 suggests that some acid was present from the commencement. Whether the lower value in Expt. 8 means that hypochlorous acid is primarily less photosensitive than chlorine water is doubtful. The presence of hypochlorite ions and also of the strong electrolyte sodium phosphate in the solution probably both play a part in lowering a. For we interpret the results of Expts. 3—7 in the sense that *strong electrolytes in general lower the efficiency of our primary photo-reaction resulting from quantum absorption.* Hydrochloric acid seems to be particularly effective, and $0{\cdot}5M$-lithium chloride more so than $0{\cdot}33M$-sodium sulphate. In this connexion, the marked retarding effect of chlorides, and particularly of hydrochloric acid, in photochemical reactions other than chlorine-water decomposition, is noteworthy. Examples are to be found in papers by Lemoine (*Ann. Chim.*, 1895, **6**, 433), Hatt (*Z. physikal. Chem.*, 1918, **92**, 513), Baur and Rebmann (*Helv. Chim. Acta*, 1922, **5**, 221), and Benrath and Obladen (*Z. wiss. Phot.*, 1922, **22**, 47, 65).

Finally, it may be remarked that the mechanism outlined above, if substantiated, will enable a clear distinction to be made (for the first time, as far as we are aware) between the *quantum efficiency* and the *quantum sensitivity* (respectively a and γ in this paper) as distinguished by Winther (*Trans. Faraday Soc.*, 1926, **21**, 608). Until this is confirmed, we have preferred to term γ the *quantum efficiency*, as is usual.

Thermochemical Relations.—For a to be unity, every absorbed quantum must cause reaction, which will probably only be the case if $Nh\nu$ is appreciably greater than the energy absorption required by the primary reaction per mol. of hypochlorous acid or of Cl_2,H_2O (Q). If they approach one another closely, then a value of a less than unity may be anticipated, although it is now generally agreed that Q may exceed $Nh\nu$ and reaction still occur in the case of absorbing molecules of particularly high individual energy content. In the present case we have (Thomsen's "Thermochemische Untersuchungen," p. 185):

$$Cl_2 + H_2O \longrightarrow 2HCl + \tfrac{1}{2}O_2 + 10270 \text{ cals.},$$
$$HClO \longrightarrow HCl + \tfrac{1}{2}O_2 + 9380 \text{ cals.}$$

Assuming that

$$O_2 \longrightarrow 2O - 140000 \text{ cals.},$$

we get

$$Cl_2 + H_2O \longrightarrow 2HCl + O - 59730 \text{ cals.},$$
$$HClO \longrightarrow HCl + O - 60620 \text{ cals.},$$

these figures corresponding to $\lambda = 475\ \mu\mu$ and $\lambda = 468\ \mu\mu$ respectively. The longest wave-length used in our work was $436\ \mu\mu$, corresponding to 65040 cals. Hence it would appear that, as far as the size of the absorbed quantum is concerned, a should be unity in all cases. It will be remembered that our values of γ only showed slight and doubtful variations with wave-length between the limits 313—436 $\mu\mu$, which is in accordance with the above.

The C reactions are both strongly exothermic, apart from any excess energy derived from the primarily absorbed quantum which the oxygen atoms may carry. We have

$$\begin{gathered} HClO + O \longrightarrow HCl + O_2 + 79380 \text{ cals.}, \\ Cl_2 + H_2O + O \longrightarrow 2HCl + O_2 + 80270 \text{ cals.} \end{gathered}$$

Finally the D reactions, with *unactivated* oxygen, would both be somewhat endothermic :

$$\begin{gathered} HClO + O_2 \longrightarrow HClO_3 - 6000 \text{ cals.}, \\ Cl_2 + H_2O + O_2 \longrightarrow HCl + HClO_3 - 5110 \text{ cals.}, \end{gathered}$$

but with the oxygen molecules carrying at any rate a proportion of the reaction energy liberated in C, their exothermic nature would appear highly probable.

Order of Reaction.—As long as the course of the reaction is represented by processes A, C, and D, the order will be between 0 and 1, increasing as the solution becomes more dilute, or as we pass from light of strongly absorbed to light of weakly absorbed wave-lengths. If, however, the solution becomes so dilute that B becomes more important than C, then n will increase still further. For the extreme case (c negligible compared with b), we have

(A) $-d[HClO]/dt = +d[O]/dt = k_a I_0 \varepsilon [HClO]$

(ε is the molecular extinction coefficient of HClO),

(B) $-d[O]/dt = 2d[O_2']/dt = k_b[O]^2$,

(D) $-d[O_2']/dt = -d[HClO]/dt = k_d[O_2'][HClO]$,

(E) $-d[O_2']/dt = k_e[O_2']$.

Whence, for the complete reaction,

$$-\frac{d[HClO]}{dt} = k_a I_0 \varepsilon [HClO]\left\{1 + \frac{k_d[HClO]}{2(k_e + k_d[HClO])}\right\}$$

which corresponds to an order greater than unity and increasing as [HClO] decreases. Any change in k_a, ε, etc., during insolation would of course complicate matters, *e.g.*, an increase in ε would decrease, or a decrease in k_a would increase, the apparent order of the reaction.

Certain experiments carried out under uniform conditions of illumination from start to finish, with titrations made at intervals, have allowed of a calculation of the *average apparent* order of the reaction by means of the equation

$$(1/C_1^{n-1} - 1/C_2^{n-1})/(1/C_2^{n-1} - 1/C_3^{n-1}) = (t_1 - t_2)/(t_2 - t_3),$$

where C_1, C_2, C_3 represent concentrations at the times t_1, t_2, t_3. The results are in Table IX.

TABLE IX.

Expt.	Solution.	Light.	$t_3 - t_1$ (hours).	C_1 (normality).	C_3	n.
1	HClO.	Unfiltered.	4	0·114	0·070	0·25
—	,,	,,	4	0·091	0·052	0·6
2	Chlorine.	,,	23·25	0·067	0·001	1·2
3	,,	,,	23·5	0·084	0·003	1·2
4	,,	,,	22·25	0·056	0·001	1·2
5	,,	436 $\mu\mu$	36·25	0·099	0·069	1·0
6	,,	365 $\mu\mu$	31	0·103	0·048	0·0

Whilst demonstrating the complexity of the photolysis, they are in general agreement with the above deductions. In (6), the absorption is complete throughout, and the rate of reaction very uniform, in spite of the 50% decrease in concentration and the gradually increasing acidity, which would be expected to lower the quantum efficiency. On the other hand, in (5), where, in spite of the partial decomposition, the absorption slightly increases during the experiment (increase in ε), and where n was found to be very close to unity, it would seem that either the concentration or, more probably, the acidity effect (decrease in k_a) must be playing a compensating part. In (1) where absorption is only complete for the ultra-violet components of the light, n increases during the course of the reaction, although the absorption of visible light is also increasing (increase in ε). Here the same acidity effect appears to enter. And in (2), (3), and (4), where the rate of decomposition falls off rapidly towards the end of the reaction, it would seem likely that both k_a (acidity) and concentration influences play a part.

Further work is in progress from several points of view on the questions raised in this paper, particularly on the marked influence of hydrochloric acid on the course of the reaction, a factor which we consider responsible for the non-reproducible nature of some of the experiments, and on the general effect of strong electrolytes on our coefficients a and d.

Summary.

(1) Data are presented on the extinction coefficients of aqueous solutions of chlorine and of hypochlorous acid, both in absence and in presence of certain electrolytes.

(2) The results are recorded of quantum efficiency measurements made during the photodecomposition of such solutions.

(3) A detailed mechanism is suggested for such photodecomposition, which attempts to correlate the nature and proportions of the decomposition products with the observed quantum efficiencies, with the variations in the extinction of the solutions, with their chlorine partial pressures, and with the order of the reaction.

(4) This mechanism permits of the efficiencies of the primary and secondary reactions being separately determined, and allows of the analysis (up to a point) of the nature of the retarding effect exerted by strong electrolytes on the photodecomposition.

The experimental work in this paper was carried out during the years 1921—1924. Of the authors, one (P. W. C.) wishes to acknowledge the help afforded by a bursary granted him by the British Cotton Industry Research Association, and another (R. E. W. M.) similarly wishes to acknowledge the grant made him by the Advisory Council of the Department of Scientific and Industrial Research. Some of the quartz apparatus employed was purchased out of a grant made to the laboratory by Messrs. Brunner Mond and Co., Ltd., to whom we express our indebtedness.

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[*Received, December* 15*th*, 1926.]

CI.—*On Active Nitrogen. Part II. Reactions with Gases.*

By ERIC JOHN BAXTER WILLEY and ERIC KEIGHTLEY RIDEAL.

IN a previous communication (J., 1926, 1804) evidence was presented for the assumption that active nitrogen represents a metastable molecule with the low mean energy content of *ca.* 43,000 cals./g.-mol. Experiments are now described upon the addition of gases—elementary, compound, and mixed—to the afterglow, and the bearing of these observations upon the energy content of active nitrogen is discussed.

The considerations underlying the various possible types of interaction between atoms and electrons noted by Franck, Klein, and Rosseland (*Z. Physik*, 1922, **4**, 41) have been extended by Franck and his co-workers to the case of interaction between excited atoms and molecules. In applying these considerations to the case of active nitrogen, the following possibilities are open:

(1) If the least radiation potential of the added gas be less than the energy of active nitrogen, the former may be stimulated to the

production of an excited molecule with the subsequent emission of its characteristic spectrum. Moreover, if its critical increment for dissociation, reaction, or decomposition also be less, chemical action may occur.

(2) If the lowest radiation potential of the added gas be greater than the energy of active nitrogen, the luminescence of the latter should be quenched to an extent depending on the nature and amount of the added gas. The excitation of certain spectra of metals, the dissociation of hydrogen examined by Franck (*Z. Physik*, 1922, **11**, 16), and the quenching of fluorescence with various gases examined by Wood (*Physikal. Z.*, 1912, **13**, 353) for mercury atoms excited by the line $\lambda = 2537$ are well-known examples of these cases.

Certain other possibilities, however, are present.

(3) The active nitrogen may react with the added gas or vapour to form a nitride, the necessary energy of activation for formation being less than the energy content of active nitrogen. If the resulting nitride be stable and its formation exothermic, the energy set free (which includes the heat of formation and the original energy content of the active nitrogen) may be dissipated as radiation—the phenomenon of chemiluminescence.

(4) Finally, reaction may take place between active nitrogen and molecules excited as in (1) to form an endothermic nitride which may subsequently undergo decomposition with the emission of radiation.

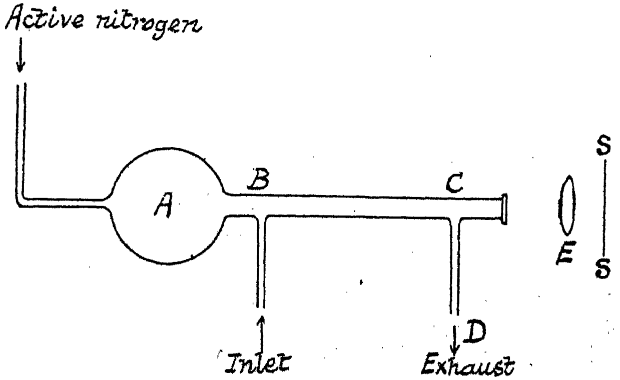
By applying these data upon the critical energy increments to observations of the effect of other gases upon the afterglow and the chemical reactions effected, we should be able to determine approximately the energy content of active nitrogen. The experiments show that with gases of critical energy increments below 55,000 cals./g.-mol. chemical action is always traceable, but it is only strong where the critical energy increment is *ca.* 43,000 cals. and under. Reliance has been placed upon chemical reaction rather than spectroscopic observations, the employment of the latter being inadvisable in view of the presence of so many possible disturbing factors, as has already been pointed out by one of us (*Nature*, 1926, **118**, 735). The latter value agrees closely with that put forward in our first paper.

EXPERIMENTAL.

Active nitrogen was led from the discharge tube through the bulb, A (Fig. 1), to the tube, BC, which was some 25 cm. long. About 2 cm. along this tube a second tube was provided for the admission of the gases whose effects were to be studied, and the mixture was drawn to exhaust at D. The end of BC remote from the active-nitrogen inlet was ground flat, and by means of a lens, E, the light in it could be focussed on the slit, SS, of a Hilger spectrometer. A series of condensing traps immersed in liquid air was placed in the exhaust line for the collection of any condensable products of the reactions taking place. The results are now given according to the considerations already advanced.

(a) *Hydrogen.* This gas is of interest in that its heat of dissociation is *ca.* 75,000—80,000 cals./g.-mol., and that it is readily activated or dissociated by collision with mercury atoms excited by the line $\lambda = 2537$. In agreement with Lord Rayleigh (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) we find that pure hydrogen has no appreciable effect upon the glow. Examination of the gases condensed by cooling in liquid air after a run of 10 hours failed to show any trace of ammonia. Since, however, the evidence for the formation of ammonia on the admixture of nitrogen and activated hydrogen is conflicting,* the nitrogen–hydrogen mixture was

FIG. 1.



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* The experiments of Wendt, Venkataramaiah, and Hirst all indicate that active hydrogen, produced either by the discharge or by Franck's method with excited mercury atoms, yields appreciable quantities of ammonia on interaction with nitrogen. On the other hand Bonhoeffer (*Z. physikal. Chem.*, 1924, **113**, 199) and Taylor (*Trans. Faraday Soc.*, 1925, **21**, 562) have failed to detect ammonia formation with active hydrogen. We have satisfied ourselves that if a stream of nitrogen at 10 mm. pressure be led into a stream of hydrogen at a point 150 mm. away from the end of the discharge tube through which hydrogen is flowing at the same pressure, appreciable quantities of ammonia are formed.

Mr. A. Caress, working in this laboratory, has recently obtained experimental evidence in support of the view that hydrogen atoms react with nitrogen to form ammonia at a catalytic metal surface but not in the homogeneous gas phase, a reaction which can be made to take place on excitation by electron collision.

passed over iodine, arsenic and sulphur (compare Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510), and also, after admission of oxygen, over phosphorus pentoxide in a weighed tube. In no case was any evidence obtained for the production of an active variety of hydrogen.

(b) *Oxygen.* This readily extinguished the luminescence with the production of heat. No evidence for the formation of nitric oxide or ozone was obtained. Also, with hydrogen–oxygen mixtures in various ratios, no indication of water formation over periods of 10 hours was obtained.

(c) *Carbon monoxide.* This gas merely dilutes the glow, behaving in this respect like nitrogen or hydrogen, as might be anticipated from the close similarity between carbon monoxide and nitrogen.

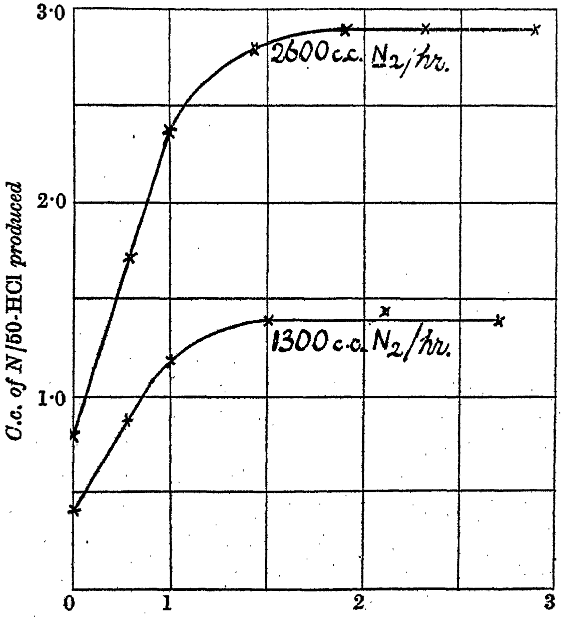
(d) *The halogens.* The characteristic blue luminosity of iodine is readily excited (compare Rayleigh, *loc. cit.*). The same holds true for bromine, the colour being brick-red. In the case of chlorine, the effect on the afterglow is much less marked; this, however, may be due in part to the fact that the spectrum of chlorine in the visible region overlaps the spectrum of the afterglow. The dissociation energies of the three halogens (in cals./g.-mol.) are: Iodine, 34,500; bromine, 46,200; and chlorine, 55,000.

In no case could any condensate containing nitrogen and halogen be obtained by cooling with liquid air (compare Noyes, *J. Amer. Chem. Soc.*, 1921, **43**, 1774).

The effect of admitting a mixture of hydrogen and a halogen to the afterglow was examined for the production of hydrogen halides, but the results were negative with both bromine and iodine. With chlorine, however, the production of hydrogen chloride, together with minute traces of ammonium chloride and small quantities of a substance giving the characteristic reactions of chloroamine, was observed. Since this was the first instance of a chemical reaction being brought about by active nitrogen, similar to a hydrogen–oxygen reaction brought about by active mercury atoms, the case was examined in some detail.

When a mixture of hydrogen and chlorine was admitted to a stream of active nitrogen and the mixture drawn to exhaust through a U-tube cooled by liquid air, the gases which condensed gave a strongly acid solution in water, even when examined so rapidly as to preclude the formation of hydrogen chloride by reaction between the chlorine and the water. An absorption tube was then constructed in such a manner that the inlet tube terminated about 3 cm. above the bottom, and 10 c.c. of 15% neutral solution of potassium iodide were frozen into it. It was then immersed in liquid air and employed as a condenser as before. At the end of the experiment, this tube was filled with nitrogen whilst still connected to the apparatus, sealed off, and warmed to allow the chlorine to be absorbed. It was then opened and the contents were washed out and titrated with neutral *N*/50-sodium thiosulphate until the iodine was removed, after which phenolphthalein was added and the whole titrated to neutrality with *N*/50-alkali, several c.c. being required. The presence of free hydrochloric acid was also proved (*a*) by titrating with *N*/50-sodium thiosulphate after addition of potassium iodide and iodate, and (*b*) by means of the hydrogen electrode.

FIG. 2.



Bubbles of 1 : 1 H_2–Cl_2 *mixture per second.*

Blank tests in which all conditions were the same as in the actual experiments, except that the nitrogen was not activated, gave no trace whatever of hydrogen chloride.

With constant nitrogen flow and constant composition of the hydrogen–chlorine mixture, the yield of hydrogen chloride was constant, and a few quantitative studies of its production were made. The results (Fig. 2) show that with a 1 : 1 mixture of hydrogen and chlorine the yield of hydrogen chloride increases with the quantity of the mixture added, but a limit is reached after which no further combination takes place.

The formation of hydrogen chloride may be ascribed to three causes: (*a*) Reduction *in situ* by the hydrogen of an unstable nitrogen chloride. (*b*) Photochemical combination of chlorine and hydrogen under the influence of ultra-violet light emitted during the decay of the active nitrogen, probably with the formation of long chains to account for the relatively high yields of hydrogen chloride. (*c*) The production, by second-type collisions, of active chlorine molecules excited to a level sufficiently high to enable them to combine with hydrogen.

The first of these is contrary to the fact that Noyes (*loc. cit.*) was unable to prepare any nitrogen chloride by the action of active nitrogen upon chlorine even under the most varied conditions of flow speeds, etc. Decomposition of an unstable halide should be prevented by the addition of a large excess of chlorine.

In the absence of measurements of the absolute intensity of the active nitrogen luminosity, little can be done directly to prove or disprove the second hypothesis. Such a determination would give the total number of quanta emitted per second per unit volume of active nitrogen. A knowledge of the intensity of the part of the afterglow spectrum which is of wave-length short enough to bring about this synthesis, relative to the whole series of bands, would then give the number of quanta available for the reaction. Application of this value to the known data for the combination of hydrogen and chlorine would give an approximate estimate as to the probable yield of hydrogen chloride.

The third hypothesis is to a certain extent capable of analysis. It is possible, upon the assumption that every collision between molecules of active nitrogen and chlorine results in the formation of hydrogen chloride through the intermediate production of an active chlorine molecule, to calculate the probable yield of the acid. The number of collisions per c.c. per second is given by

$$n = 2\nu_1\nu_2(\sigma_1 + \sigma_2)^2\sqrt{2\pi kT(m_1 + m_2)/m_1m_2}$$

where ν_1 and ν_2 represent the number of molecules entering per second of active nitrogen and chlorine, respectively, σ_1 and σ_2 their diameters, and m_1 and m_2 their masses, and k and T have their usual significance. In a typical experiment a flow speed of 2600 c.c./hr. of nitrogen at *N.T.P.* was maintained, 1·5% of active nitrogen was present, and a 1 : 1 mixture of hydrogen and chlorine was admitted at the rate of $6{\cdot}2 \times 10^{-3}$ c.c./sec. 3·04 C.c. of *N*/50-hydrochloric acid were obtained in 30 minutes.

Hence $\nu_1 = 1{\cdot}5 \times 10^{-2} \times 2{\cdot}7 \times 10^{19} \times 2600/3600 = 2{\cdot}9 \times 10^{17}$;
$\nu_2 = 3{\cdot}1 \times 10^{-3} \times 2{\cdot}7 \times 10^{19} = 8{\cdot}3 \times 10^{16}$;
$\sigma_1 + \sigma_2 = 6 \times 10^{-8}$; $k = 1{\cdot}37 \times 10^{-16}$;
$m_1 = 1{\cdot}66 \times 28 \times 10^{-24}$; $m_2 = 1{\cdot}66 \times 71 \times 10^{-24}$.

Substituting in the equation, we obtain $15{\cdot}2 \times 10^{24}$ collisions/sec. between molecules of active nitrogen and chlorine.

Since the number of chlorine molecules entering per second is $8{\cdot}3 \times 10^{16}$, we see that every one will be hit several times every second; hence we may assume that all the chlorine molecules present are activated at least once.

The number of collisions between the hydrogen and chlorine molecules is similarly calculated to be $6{\cdot}2 \times 10^{24}$/sec.

Hence the number of collisions between the active nitrogen and chlorine molecules and between the chlorine and hydrogen is sufficient to warrant the assumption that yields of hydrogen chloride comparable with the concentration of active nitrogen should be obtained. This is the case, since the yield observed gives $2{\cdot}05 \times 10^{16}$ molecules/sec., whereas the active nitrogen flow is $2{\cdot}9 \times 10^{17}$ molecules/sec.

Hence we have considerable evidence that the production of hydrogen chloride is due to the formation of excited molecules of chlorine.

In searching for a reason why hydrogen chloride should be produced whilst neither hydrogen bromide nor iodide is formed, we may note that we are dealing with the stimulation only of the halogen to form an excited molecule, a condition comparable with the photochemical union between hydrogen and the halogens rather than with the thermochemical union. The photochemical union of the halogens is conditioned either by the heat evolution of the reaction $X + H_2 = HX + H$, as postulated by Nernst, or by that of the reaction $X_2' + H_2 \longrightarrow XH + H + X$, if the view be taken that the excited halogen molecule (X_2') is the reactive molecule. It is well known that the photochemical combination of hydrogen with chlorine, but not that of hydrogen with bromine or iodine, takes place at the ordinary temperature when the halogens are excited only to their threshold values for reaction, *i.e.*, in the visible portion of the spectrum. The fact that the halogens on excitation with active nitrogen yield banded rather than line spectra lends support to the hypothesis that the primary chemical reaction in the photochemical combination of a halogen with hydrogen is a reaction between an excited molecule of the halogen and hydrogen rather than the dissociation of the excited molecule into atoms with subsequent reaction. It does not, however, distinguish between the two possible reactions (1) $X_2' + H_2 \longrightarrow HX + HX'$, and (2) $X_2' + H_2 \longrightarrow HX + H + X$, although, from analogy with the thermal combination of hydrogen and bromine and from the existence of chains in the hydrogen–chlorine reaction, the reaction (2) appears more plausible than (1).

(e) *The hydrogen halides.* The halides HI, HBr, HCl form an interesting series in that the energies of activation for decomposition rise from the iodide to the chloride. From Bodenstein's data (*Z. Physik*, 1899, 29, 295), the energy of activation for the thermal decomposition of hydrogen iodide can be computed as $E_{2HI} =$ 45,700 cals. For the other reactions, such data are not available, but it may be noted that hydrogen bromide decomposes in the homogeneous gas phase quite rapidly over the temperature range 400—750° K., which would indicate an energy of activation of about 40,000—50,000 cals./g.-mol. For hydrogen chloride, much higher temperatures are necessary (*ca.* 1400° K.) which would yield a value of $E_{2HCl} =$ *ca.* 90,000. If we compare the threshold radiation wave-lengths at which the percentage decompositions for the three halides are approximately identical, we obtain $\lambda = 4000$, 2800, and 2200 Å. for the iodide, bromide, and chloride, respectively. Since $E_{2HI} = 45,700$, those of the others must be of the order $45,700 \times 40/28$ and $45,700 \times 40/22$ or 65,000 and 83,000, respectively. We may assign values of the order of $E_{2HI} = 45,700$, $E_{2HBr} = 50,000$, $E_{2HCl} = 90,000$ without serious error. We should anticipate that both hydrogen iodide and hydrogen bromide might suffer decomposition, but not hydrogen chloride. This is found to be the case; the typical spectra of iodine and bromine were noted, whilst in the liquid-air trap both free halogen, ammonium halide, and traces of halogeno-amine were obtained. The reaction was *much* less marked with hydrogen bromide than with hydrogen iodide.

(f) *The oxides of nitrogen.* Both nitric oxide and nitrous oxide are of importance in this connexion. As has already been indicated (Part I, *loc. cit.*), the critical increment of nitric oxide is certainly below 55,000 cals., and in consequence the gas reacts with active nitrogen, undergoing decomposition to nitrogen and oxygen. In the case of nitrous oxide, we can, from the data of Hunter (*Z. physikal. Chem.*, 1905, **53**, 441) and of Hinshelwood (*Proc. Roy. Soc.*, 1924, **106**, 284) for the homogeneous bimolecular reaction, calculate an energy of activation of 60,300 cals./g.-mol. This gas was examined in the present experiments and did not affect the glow of active nitrogen. Moreover, when the gases, after admission of the nitrous oxide, were mixed with nitric oxide below the point where the afterglow ceases to be visible, no evidence of the formation of nitrogen peroxide in the liquid-air trap was found, indicating that no decomposition of the nitrous oxide had taken place

We have noted that hydrogen chloride, hydrogen, and nitrous oxide, with energies of decomposition of the order of 90,000, 85,000, and 60,000 cals./g.-mol., respectively, do not affect the afterglow, and we may therefore conclude that the energy of active nitrogen is below these limits. Other gases of relatively large critical energy increments were likewise examined for their effect on the afterglow; these included water vapour, carbon dioxide, and carbon monoxide, with energies of activation of the order of $E_{2CO_2 \rightarrow 2CO + O_2} = 120,000$ cals./g.-mol. and $E_{2H_2O \rightarrow 2H_2 + O_2} = 110,000$ cals./g.-mol. In neither case was any effect other than a dilution observed.

Careful search for oxygen (by the admission of nitric oxide) and for cyanogen compounds in the former case, and for water and formaldehyde in a carbon monoxide–hydrogen mixture, revealed no evidence of chemical reaction.

We have seen that among the gases which are raised to a chemically reactive state we may include the halogens, and in the case of chlorine, of which the lowest critical increment for reaction with hydrogen is some 55,000 cals./g.-mol., only a part of the active nitrogen appears to be effective in promoting chemical action. This would set 55,000 cals. as the upper limit for the energy content of active nitrogen, whilst the experiment with nitrous oxide indicates that 60,000 cals. is well above the maximum.

Adopting a value of 150,000 cals. for the latent heat of evaporation of carbon (Thiel and Ritter, *Z. anorg. Chem.*, 1923, **132**, 151), we obtain for the linkage C–H (Fajans, *Ber.*, 1920, **53**, 643) a value of *ca.* 80,000 cals.; we should accordingly anticipate that methane would not be affected by active nitrogen. Lord Rayleigh (*Proc. Roy. Soc.*, 1915, **91**, 317) was of the opinion that methane underwent slight decomposition, a view to which König and Elöd (*Ber.*, 1914, **47**, 516) could not subscribe. Since small traces of other hydrocarbons readily react with active nitrogen, it is necessary to ensure their absence from the gas, and we have accordingly prepared pure methane from carbon monoxide and hydrogen by passage over a diatomaceous earth–nickel catalyst. This gas, which, after seven fractionations from liquid air, was free from carbon monoxide, did not affect the glow of active nitrogen, and no hydrogen cyanide could be detected in the gases after admixture of the methane. It may be observed that methane will undergo decomposition with a critical increment of only 55,000 cals. on a hot platinum wire (Schwab and Pietsch, *Z. physikal. Chem.*, 1926, **121**, 189) and a surface reaction between active nitrogen and methane is thus not impossible under the right conditions.

Ammonia is readily decomposed by active nitrogen into nitrogen and hydrogen; the critical increment here is probably quite low.

Conclusions.

In all the cases so far examined, chemical action as a result of second-type collisions, either between active nitrogen and the gas introduced or else as a "sensitised" reaction, occurs only when the critical increment of the second gas for the appropriate reaction is below 55,000—60,000 cals./g.-mol., and is strongest when this is about 45,000 cals./g.-mol. This is obviously a measure of the energy of active nitrogen, and is not incompatible with the view that in the afterglow we probably have a species of statistical equilibrium among three types of active molecules, some above, some below, and the majority upon the 2-volt level, an opinion which is supported by the spectroscopic evidence upon the afterglow. The three series of bands into which the true afterglow spectrum can be divided have intensities roughly in the ratio 1 : 2 : 1 for the red, yellow, and green, respectively, and the upper limit of the last-named bands coincides well with that observed for the limiting increment for reaction with active nitrogen (55,000—60,000 cals./g.-mol.). Moreover, if, as a first approximation, we regard these intensities as giving the relative concentrations of the three species, we see that with a gas of critical increment of, say, 55,000 cals./g.-mol., the extent of the reaction should be about one-fourth of that observed, all other conditions being left constant, with a gas for which the critical increment is 43,000 cals./g.-mol. and below. In the case of hydrogen and chlorine the yield of hydrogen chloride is about 1/14th of the active nitrogen concentration, and while the point cannot for obvious reasons be stressed, this observation is nevertheless significant.

These reactions are of course selective in nature and do not directly give a mean value for the energy of the active nitrogen, such as is obtained by the calorimetric method. Making due allowance for other necessary considerations as indicated, we see that the value originally given for the energy of active nitrogen is amply confirmed.

It is also interesting to note that Aakeson (*Lunds Univ. Arsskr.*, 1916, **12**, No. 11) found that 1·7-volt electrons undergo inelastic collision with nitrogen molecules, and whilst this value is most probably not correct to ± 1 volt, since no correction was applied for initial velocity, the existence of a level in the molecule at about that to be expected from an evaluation of the energy of active nitrogen would appear to be established.

It would here appear advisable, in view of the criticisms which have been directed against our contentions as to the energy content and nature of active nitrogen, to restate our case *in extenso* and effect such agreement as is possible between our observations and the postulates of the spectroscopists (compare Johnson, *Nature*, 1927, **119**, 9).

In the preceding paper, on the assumption that one molecule of active nitrogen excites but one molecule of nitric oxide on reaction according to the schemes $N_2' + NO \longrightarrow NO'$ and $NO' + NO \longrightarrow N_2 + O_2$, it was shown that the calorimetric energy content of active nitrogen was equivalent to *ca.* 2·0 volts. In this paper, we have shown that chemical reaction is only effected by transfer of energy by second-type collisions from the active nitrogen to other gases when the requisite energy of activation lies below *ca.* 2·1 volts.

It is hoped to communicate similar conclusions from experiments on the catalytic decay of active nitrogen at the surface of metallic filaments, and from application of the Nernst heat theorem to the observations of one of us (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 260) on the iron nitride content of the vapours in an iron–nitrogen arc. It thus appears that for the purposes of chemical reaction active nitrogen only liberates energy equivalent to a 2·0-volt fall. We have regarded this as the total energy content of active nitrogen, for, as was pointed out in our first communication, there appears to be no reason why we should postulate the existence of several 2·0-volt falls in each molecule of active nitrogen. If, for example, the true energy content of active nitrogen is equivalent to 10 volts, then it will be necessary to postulate that one molecule can excite five nitric oxide molecules, transferring at each collision energy equivalent to *ca.* 2·0 volts. The same is true for the variety of chemical reactions recorded here: in no case do we find the active nitrogen transferring energy at one time equivalent to 4, 6, 8, or 10 volts, but always in 2-volt steps. Such steps in energy transfer apparently do not occur with excited mercury atoms, but if this suggestion for the reconciliation of spectroscopic and chemical data be true, it appears probable that the existence of successive 2-volt levels of some kind in the decay of active nitrogen should be capable of observation by spectroscopists.

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CAMBRIDGE. [*Received, December 1st, 1926.*]

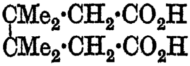
CII.—*The Effect of* gem-*Dialkyl Groups on the Formation and Stability of the Anhydrides of Dicarboxylic Acids.*

By Ernest Harold Farmer and Jacob Kracovski.

Reference has been made by various authors to the modifying effect of substituent alkyl groups on the ease of formation and the stability of the anhydrides of dicarboxylic acids. Auwers and Meyer (*Ber.*, 1890, **23**, 101), referring to the marked effect of alkyl substituents in the succinic and glutaric series and the failure of adipic acid to yield an anhydride, asked whether "durch Einführung mehrerer Methylgruppen in das Molekül der Adipinsäure eine Säure erhalten wird, welche der Anhydridbildung fähig ist," and Ingold (J., 1921, **119**, 308), dealing with the effect of *gem*-dialkyl groups on ring formation, pointed out that the same effect is equally apparent in heterocyclic ring-formation (lactones and glutaric anhydrides). It is clear from numerous incidental observations that in the succinic and glutaric series the ease of formation and the stability of anhydrides tend to increase with the number and size of substituted alkyl groups; even in the malonic series, in which the anhydrides, although capable of reacting as simple molecules, are almost certainly multimolecular, the correspondence of increased stability with increased substitution has been observed. How far this tendency extends is uncertain; many highly-substituted anhydrides of these series have not yet been obtained and at present comparisons are legitimate probably only between the members of a series. With members of different series, the hetero-structure of the ring presents difficulty; the extent to which the oxygen atom may relieve or transmit strain is unknown. Although in general an oxygen atom in a ring appears to function much as a carbon atom (leading to stability in the five- and six-membered anhydrides), yet there is a difference between homocyclic and heterocyclic rings in that the stability of the six-membered glutaric anhydrides increases with further substitution (compare Ingold, J., 1921, **119**, 952).

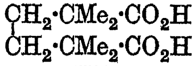
Any general attempt to compare anhydrides and homocyclic rings is confronted, when the adipic series is reached, by the problem of the close approach or the overlapping of the terminal groups. The possibility of obtaining stable, unimolecular anhydrides in this and higher series has not been explored. Consequently the nature of the factors tending chiefly towards stability, whether angular modifications as in the lower homocyclic rings, multiplanarity, re-entrant angles, or accommodative power of the oxygen atom, is quite unknown. The anhydrides of various mono-, di-, and trialkyladipic acids have been obtained by Blanc and other workers. All of these pass into the corresponding ketones on heating, but no evidence as to their complexity is offered.

We have examined the anhydrides of adipic acid and of β-methyladipic acid. Both of these substances may be obtained in the pure condition and they are definitely unimolecular. They are distillable at low pressures without decomposition, but pass readily into the corresponding acids by absorption of moisture from the atmosphere. For the purpose of testing whether any considerable degree of stability may be conferred on the anhydrides of this series by the introduction of alkyl groups, two tetramethyladipic acids have been synthesised (J., 1926, 2318). Each of these acids (I and II) yields a crystalline, unimolecular anhydride. That of the ββ′β′-acid is partly converted into the ketone (III) on prolonged heating and is readily hydrolysed by hot water. The highly crystalline anhydride of the αα′α′-acid shows no tendency to pass into the corresponding ketone; it may be prepared by prolonged heating of the acid and is not hydrolysed by boiling water or aqueous sodium carbonate. Moreover, it yields an anilic acid with much greater difficulty than its isomeride. The two substances correspond roughly in properties with glutaric and di- or tri-methylglutaric acids respectively. Therefore it is evident, not only that substitution produces a considerable change in the stability of anhydrides in this series, but also that equivalent substitution causes effects varying with the position of substitution.



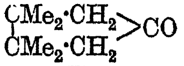
$$\begin{array}{l} CMe_2\cdot CH_2\cdot CO_2H \\ CMe_2\cdot CH_2\cdot CO_2H \end{array}$$

(I.)



$$\begin{array}{l} CH_2\cdot CMe_2\cdot CO_2H \\ CH_2\cdot CMe_2\cdot CO_2H \end{array}$$

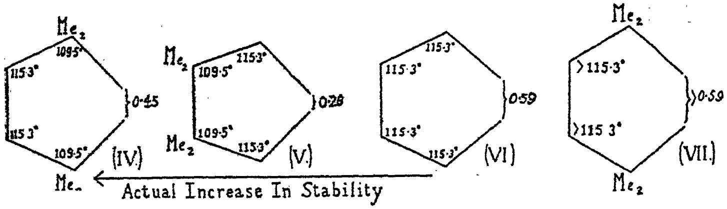
(II.)



$$\begin{array}{l} CMe_2\cdot CH_2 \\ CMe_2\cdot CH_2 \end{array}\!\!>CO$$

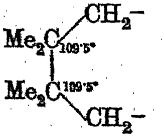
(III.)

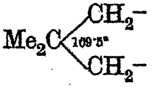
The abnormal effect of an α-substituent was observed by Ingold in studying ring-formation from bromo-α-methylglutaric acid (J., 1925, **127**, 387); here the introduction of an α-methyl group greatly hinders the formation of a *cyclo*propane ring. The abnormality was attributed to a " branched-chain " (volume) effect tending to open the valencies of the chain at the β-carbon atom. Short (*Chem. News*, 1926, **133**, 145), however, in criticising the suitability for comparing ring-forming tendencies of the method employed in this and other similar cases—that of hydrogen bromide removal from α-brominated esters—states that the inferior yield of the cyclic acid is probably to be attributed, in part, to the polar factors which control the ease with which the components of hydrogen bromide are removed. If the ready formation and superior stability of αα′α′-tetramethyladipic anhydride are attributable to the " opening " effect caused by branching of the chain at the α-carbon atoms, it would appear that the properties of αα$\alpha'\alpha'$-tetramethyladipic acid in relation to adipic acid are in keeping with the " terminal approach" explanation of the inferior ring-forming capacity, and anhydride stability of the latter. Further, the approach in stability of ββ$\beta'\beta'$-tetramethyladipic anhydride towards that of ββ-dimethylglutaric acid would seem to have a rough correspondence with the almost identical distances (using Ingold's angular value for $CMe_2<$) between the terminal carbon atoms of the tetramethylbutane- (VIII) and dimethylpropane- (IX) chains. It would seem, however, that if a " branched-chain " effect is imagined to result from α-substitution, a similar effect might quite well be caused by the proximity of the *gem*-groups at the β-carbon atoms of ββ$\beta'\beta'$-tetramethyladipic acid. If the carbon atoms of the adipic chain are regarded as uniplanar, then on the basis of Ingold's angular values for $CH_2<$ and $CMe_2<$, the approach of the carboxyl carbon atoms may be indicated as in figures IV, V, and VI. The relative magnitude of the " approach " figures does not correspond with the observed ease of formation and stability of the anhydrides and no better agreement is to be obtained by regarding a " branched-chain " effect (Fig. VII) as operative in the α-substituted acid. It is clear from such representations of members of the same and of different series of dicarboxylic acids that the powerful effect of *gem*-groups in promoting anhydride formation is not to be accounted for purely on the basis of tetrahedral angular modifications in a uniplanar carbon chain.



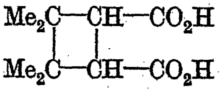
The above-mentioned approximation of the distances separating the terminal carbon atoms of the systems (VIII) and (IX) would suggest comparable tendencies towards *cyclo*butane ring-formation.

(VIII.)





(IX.)



(X.)

By the action of alcoholic potash on α-bromo-ββ$\beta'\beta'$-tetramethyladipic ester, 25% of the latter suffered replacement of bromine by hydrogen. The remaining material appeared to undergo severe degradation, the products of which escaped identification; no trace of the *cyclo*butane acid (X) could be isolated. Attempts to prepare this cyclic acid from di*iso*propylidenesuccinic acid have likewise been unsuccessful. In view of the wide difference between the extents of cyclisation achieved with αα′-dicarboxyadipic ester (100%; Perkin, J., 1887, **51**, 18) and α-bromoadipic ester (1·5%; Ingold, J., 1921, **119**, 954) these results are possibly of little significance as an index to ring-forming capacity.

Other alkylated dicarboxylic acids are at present being examined.

EXPERIMENTAL.

Tetramethyladipic Acids.—These were obtained by electrolysis (Farmer and Kracovski, J., 1926, 2318). Since only about 12 g. of the ββ′β′-acid could be accumulated, the experiments with this substance were of necessity carried out with small amounts of material.

Anhydride of ββ′β′-*Tetramethyladipic Acid.*—Tetramethyladipic acid was heated for about 2 hours with three times the quantity of acetic anhydride theoretically required. The product was evaporated in a vacuum over caustic potash; a solid was then obtained which crystallised from petroleum (b. p. 60—80°) in long, colourless, flat needles, m. p. 189° (Found: C, 65·2; H, 8·55. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%). The anhydride, which was very soluble in benzene, and moderately easily soluble in ether or petroleum, passed into the original acid (m. p. 207—208°) on warming with water. The molecular weight, determined cryoscopically in benzene, showed it to be of simple constitution (Found: *M*, 188. Calc.: *M*, 184).

The *anilic acid,* formed by treating a benzene solution of the anhydride with the calculated quantity of aniline dissolved in the same solvent, separated from hot chloroform as a crystalline powder (Found: C, 68·8; H, 8·1; *M*, monobasic, 281. $C_{16}H_{23}O_3N$ requires C, 69·3; H, 8·3%; *M*, 277).

1 : 1 : 2 : 2-*Tetramethyl*cyclo*pentan-4-one.*—The anhydride of the ββ′β′-acid (2 g.) was refluxed for some time and then allowed to distil slowly. A small quantity of an oil (b. p. 186—189°) of strong camphoraceous odour was obtained. This substance readily yielded a semicarbazone, which crystallised from hot aqueous alcohol in shining plates, m. p. 223°. Comparison of the latter with a specimen (m. p. 223°) prepared by Francis and Willson's method (J., 1913, **103**, 2245) proved the identity of the two.

The anhydride of αα′α′-*tetramethyladipic acid* was obtained in similar fashion to the ββ′β′-anhydride. The crude, solid anhydride, which was moderately easily soluble in benzene or ether but only very sparingly soluble in petroleum, crystallised from benzene–petroleum in long, colourless prisms, m. p. 166° (Found: C, 64·9; H, 8·5; *M*, cryoscopic in benzene, 180. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%; *M*, 184). The *anilic acid* separated when a benzene solution of the calculated quantities of anhydride and aniline was heated and then kept. It was insoluble in water, but crystallised from hot chloroform in needle clusters, m. p. 218° (Found: C, 68·6; H, 8·4; *M*, monobasic, 282. $C_{16}H_{23}O_3N$ requires C, 69·3; H, 8·3%; *M*, 277). The anhydride was unaffected by boiling with water or even sodium carbonate solution. It dissolved, however, on boiling with strong caustic potash solution; acidification of the product precipitated the corresponding *ααα'α'*-acid (m. p. 191°). Slow distillation of the anhydride failed to yield the corresponding cyclic ketone, the substance distilling unchanged. Prolonged heating of the acid, however, prior to distillation caused partial conversion into the anhydride.

Anhydride of β-*Methyladipic Acid.*—β-Methyladipic acid, obtained by the oxidation of 1-methyl*cyclo*hexan-4-ol, was treated with acetic anhydride as above. The acetic acid and excess of acetic anhydride were removed at 15 mm. pressure; the syrupy liquid so obtained distilled at 165°/1 mm. without decomposition. The pure anhydride is a colourless syrup which readily hydrolyses in moist air (Found: C, 59·0; H, 7·15; *M*, cryoscopic in benzene, 140. Calc.: C, 59·15; H, 7·0%; *M*, 142).

The anhydride of adipic acid, obtained as above, was a solid, m. p. 97°. It distilled without decomposition at 1 mm. (Found: *M*, cryoscopic in benzene, 130. Calc.: *M*, 128).

*Ethyl α-Bromo-*ββ*β'*β'*-tetramethyladipate.*—The ββ*β'*β'-acid (3 g.) was converted into the acid chloride by warming with the requisite amount of phosphorus pentachloride. Bromine (1 mol.) was gradually added to the product. When the absorption, which took place readily, was complete, the mixture was poured into well-cooled alcohol. After 12 hours, the bromo-ester was precipitated by means of water and obtained as a yellow oil. It was not distilled, owing to the small quantity available, but was kept for several days in an evacuated desiccator before being analysed (Found: Br, 22·8. $C_{14}H_{25}O_4Br$ requires Br, 23·7%).

Action of Concentrated Caustic Alkali Solution on Ethyl Bromotetramethyladipate.—The bromo-ester (5 g.) was warmed and then poured into boiling 6*N*-methyl-alcoholic potassium hydroxide (20 c.c.). Potassium bromide separated at once. Heating was continued for a short time; the product was then cooled, diluted with absolute alcohol (40 c.c.), and filtered. The solid material was washed with alcohol until only inorganic salts remained, the washings being added to the filtrate. Free caustic alkali was removed from the filtrate by saturating it with carbon dioxide and filtering. The alcoholic filtrate was evaporated to dryness and the residue was treated several times with water and evaporated to dryness. A solution of the final residue in a small amount of water was filtered through a wet filter-paper to remove a small amount of neutral oil and then acidified with dilute hydrochloric acid, ββ$\beta'\beta'$-tetramethyladipic acid being precipitated; a further small quantity separated when the acid solution was concentrated, the total yield (allowance being made for the slight deficit of bromine in the bromo-ester employed) being 25% of the material taken. The filtrate was finally evaporated to dryness in a vacuum, and the residue extracted with acetone. By this means a yellow syrup was obtained which, absence of severe degradation being assumed, represented about 50% of the material taken. After standing for nearly a year, the syrup deposited an acid which was readily soluble in water and separated from acetone–petroleum in colourless prisms, m. p. 212°. Owing to the very small quantity obtained, the acid could not be identified. Its low equivalent showed, however, that it was not the *cyclo*butane acid (X).

The residual syrup could not be solidified. It was distilled to free it from traces of inorganic matter, the distillate being collected in three portions. None of these reduced alkaline permanganate solution, and each had an equivalent weight and a carbon content much lower than those of the *cyclo*butane acid or hydroxytetramethyladipic acid. The syrup was almost certainly a mixture of acids, probably produced by severe degradation of tetramethyladipic acid.

The authors desire to acknowledge grants from the Government Grant Committee of the Royal Society (E. H. F.) and the Chemical Society (to J. K.) towards the cost of this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, December 2nd,* 1926.]

CIII.—*The Condensation of* p-*Hydroxybenzoic Acid with Chloral.*

By FREDERICK DANIEL CHATTAWAY and FERNANDO CALVET Y PRATS.

IT has recently been shown (J., 1926, 2720) that *p*-nitrophenol reacts with chloral in presence of concentrated sulphuric acid in a complicated and unexpected way, the final product being anhydro-

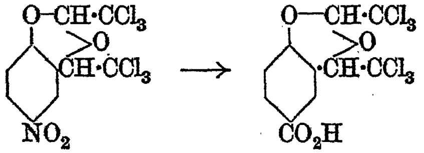
5-nitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I), the constitution of which was shown by its yielding 5-nitro-2-ethoxyphenylglycollic acid on treatment with alcoholic potash.

In similar circumstances, chloral reacts equally readily with *p*-hydroxybenzoic acid, giving a very stable and well-crystallised product, 2 mols. of the aldehyde condensing with 1 mol. of the acid, with loss of a molecule of water:

$$C_7H_6O_3 + 2CCl_3{\cdot}CHO - H_2O = C_{11}H_6O_4Cl_6.$$

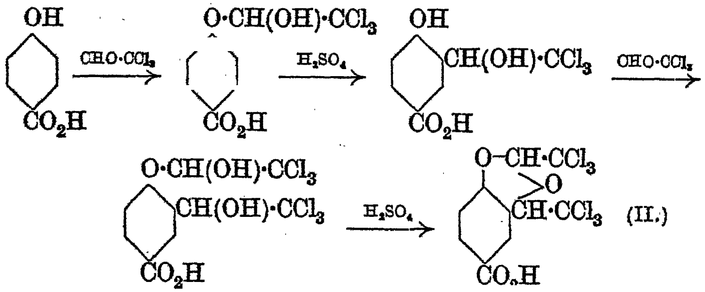
The constitution (II) of the compound formed is similar to that of the condensation product (I) yielded by *p*-nitrophenol, since it can also be formed from the latter by replacement of the nitro-group by carboxyl through the amino- and the cyano-group.

(I.)



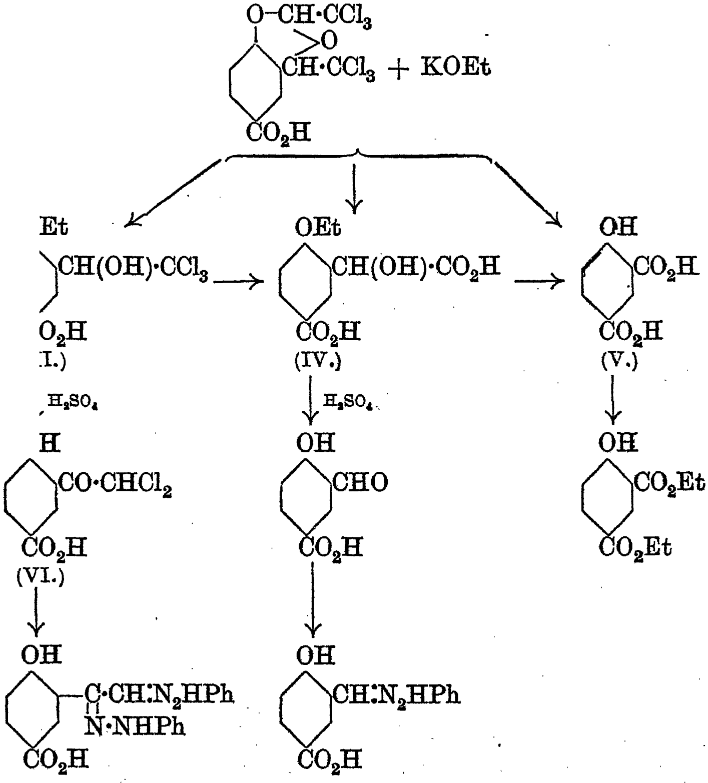
(II.)

Since in the formation of the compound from chloral and *p*-hydroxybenzoic acid the carboxyl group remains unaffected, a condensation with the phenolic hydroxyl must first occur and be followed by intramolecular rearrangement. The hydroxyl group being thus re-formed, a second condensation of the same type must occur and be succeeded by elimination of water, thus,



the final product being *anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene.*

Its constitution is confirmed by its behaviour with alcoholic potash, with which it yields a mixture of *5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene* (III), *5-carboxy-2-ethoxyphenylglycollic acid* (IV), and *2-hydroxy-1:5-isophthalic acid* (V). These compounds were identified as shown in the following scheme:



EXPERIMENTAL.

Preparation of Anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (II).—(a) *By condensation of* p-*hydroxybenzoic acid and chloral.* A solution of 50 g. of *p*-hydroxybenzoic acid (1 mol.) and 150 g. of chloral hydrate (3 mols.) in 500 c.c. of concentrated sulphuric acid was kept at the ordinary temperature, with frequent shaking, for 3 days. The liquid had then become a pulp owing to the separation of the condensation product mixed with metachloral formed by the action of sulphuric acid upon the excess of chloral present (Byasson, *Compt. rend.*, 1880, **91**, 1071). The whole was poured into about 3 litres of water containing ice, and the solid which separated was filtered off and dried on the water-bath. The condensation product was extracted in a Soxhlet apparatus with ether, in which metachloral is insoluble. The ethereal solution was dried, the ether distilled off, and the condensation product obtained by crystallising the colourless, crystalline residue (yield, 46 g.) three times from ether–light petroleum.

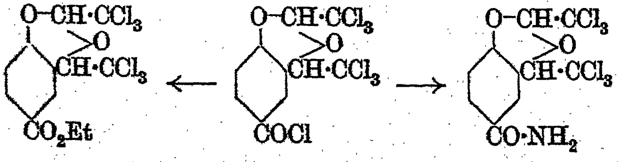
It is insoluble in water but moderately easily soluble in hot alkaline solutions. It dissolves easily in the ordinary organic solvents such as ether, alcohol, benzene, and acetic acid and separates from any of these in colourless needles, m. p. 225·5—226·5° (Found: C, 32·1; H, 1·6; Cl, 51·4. $C_{11}H_6O_4Cl_6$ requires C, 31·8; H, 1·4; Cl, 51·3%).

(b) *From the corresponding 5-nitro-compound* (I) *through the 5-amino- and 5-cyano-derivatives.* Anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (10 g.), obtained by reduction of the corresponding nitro-compound (I) (J., 1926, 2725), was suspended in a mixture of 40 c.c. of concentrated hydrochloric acid and 180 c.c. of water and diazotised by adding, during 2 hours, the requisite amount of sodium nitrite dissolved in 30 c.c. of water, the temperature being kept at — 5° to — 10°. The diazotised solution was poured slowly into a concentrated solution of 40 g. of copper sulphate and 50 g. of potassium cyanide in about 100 c.c. of water kept at 45—50°. (If the temperature is allowed to rise above this limit, a considerable amount of tarry matter is formed.) The *nitrile,* which separated on cooling as a microcrystalline mass, was extracted with ether. A yield of 2·1 g. was obtained.

Anhydro-5-cyano-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene is an odourless solid which is not volatile in steam. It is insoluble in water, sparingly soluble in low-boiling petroleum, and easily soluble in boiling ether and alcohol. It is best recrystallised from ether–light petroleum, from which it separates in colourless needles, m. p. 159·5—160·5° (Found: Cl, 53·95. $C_{11}H_5O_2NCl_6$ requires Cl, 53·8%).

The nitrile was easily hydrolysed to the corresponding acid (II) by heating it for a short time with somewhat dilute sulphuric acid. A mixture of 1·3 g. of the nitrile, 30 c.c. of water, and 45 c.c. of concentrated sulphuric acid was heated to gentle boiling for about 20 minutes. On cooling and diluting the solution with water, the acid separated as a microcrystalline solid. It crystallised from warm ether–light petroleum in colourless needles (yield, 1 g.), m. p. 226°, identical with those obtained in method (a) (Found: Cl, 51·1%).

The Ethyl Ester, Acid Chloride, and Amide of Anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene.



—The *ethyl* ester was prepared by saturating a cooled and concentrated alcoholic solution of the acid with dry hydrogen chloride and heating it in a sealed tube for some hours. The ester separated in colourless crystals on cooling. It was recrystallised from hot alcohol, in which it was moderately easily soluble and from which it separated in small, colourless, rhombic plates, m. p. 100·5—101·5° (Found : Cl, 48·3. $C_{13}H_{10}O_4Cl_6$ requires Cl, 48·1%).

The ester was also obtained by boiling the acid chloride, described below, with alcohol.

The *acid chloride* was obtained by gently heating the acid with an excess of phosphorus pentachloride and pouring the mixture over ice. It is very easily soluble in ether and very sparingly soluble in petroleum. It separates from ether–light petroleum in colourless, compact crystals, m. p. 98—102° (Found : Cl, 56·5. $C_{11}H_5O_3Cl_7$ requires Cl, 57·3%).

The *amide*, obtained by gently heating the acid chloride with a mixture of equal parts of strong ammonia solution and alcohol, was easily soluble in boiling alcohol, from which it separated in long, colourless prisms, m. p. 195·5—197° (Found: Cl, 51·2; N, 3·2. $C_{11}H_7O_3NCl_6$ requires Cl, 51·4; N, 3·4%).

*Action of Alcoholic Potassium Hydroxide upon Anhydro-5-carboxy-2-*βββ*-trichloro-*α*-hydroxyethoxy-1-*βββ*-trichloro-*α*-hydroxyethylbenzene.* —*Isolation of 5-carboxy-2-ethoxy-1-*βββ*-trichloro-*α*-hydroxyethylbenzene* (III). 20 G. of the acid (1 mol.) were added gradually to a hot solution of 48 g. of potassium hydroxide (18 mols.) in 200 c.c. of alcohol, and the mixture was gently boiled for ½ hour. Boiling water (200 c.c.) was added, and the alcohol distilled in steam. The dark red solution thus obtained deposited, on cooling, the potassium salt of 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene in colourless, thin, flaky plates. These were filtered off and treated with dilute hydrochloric acid. The *acid*, isolated by means of ether and obtained as a crystalline, colourless mass, separated from warm ether–light petroleum in small, compact crystals (yield, 8·1 g.), m. p. 124—126° (Found : C, 41·9; H, 3·5; Cl, 33·8. $C_{11}H_{11}O_4Cl_3$ requires C, 42·15; H, 3·6; Cl, 33·9%).

It is very sparingly soluble in water or petroleum and easily soluble in ether or alcohol. It forms with alkalis colourless salts which are sparingly soluble in water.

*Identification of 2-hydroxy-1 : 5-iso*phthalic acid (V). The dark red mother-liquor from the preceding potassium salt was acidified with hydrochloric acid. The acid set free, which in part crystallised, was extracted with ether. Partial evaporation of the ether and addition of a little light petroleum gave 3·2 g. of a microcrystalline product, consisting mainly of 2-hydroxy-1 : 5-*iso*phthalic acid. As it was difficult to separate this acid in a pure condition, it was identified by conversion into its *ethyl* ester. This, after two crystallisations from methyl alcohol, melted sharply at 52·5° (Found: C, 60·2; H, 6·1. $C_{12}H_{14}O_5$ requires C, 60·4; H, 5·9%).

Identification of 5-carboxy-2-ethoxyphenylglycollic acid (IV). On allowing the ethereal mother-liquor from which the 2-hydroxy-1:5-*iso*phthalic acid had separated to evaporate spontaneously, an acid crystallised in colourless, silky needles, but in too small quantity to admit of complete purification. It was shown to be mainly 5-carboxy-2-ethoxyphenylglycollic acid in the following way. A solution of the acid (1·6 g.) in 3 c.c. of concentrated sulphuric acid was heated on a water-bath for 10 minutes, cooled, and poured into water. The product, isolated by means of ether, was a brown, crystalline solid which sublimed in colourless needles; these softened at 235°, melted at 244°, and agreed in properties with 5-carboxy-2-hydroxybenzaldehyde (Tiemann and Reimer, *Ber.*, 1876, 9, 1274). It dissolved easily in hot water, and the solution gave a yellow colour with sodium hydroxide and a dark red colour with ferric chloride. It reacted with semicarbazide, yielding a well-crystallised semicarbazone.

The *phenylhydrazone*, which separated as a yellow solid when phenylhydrazine was added to a hot aqueous solution of the aldehyde, crystallised from boiling alcohol, in which it was moderately easily soluble, in yellow needles, m. p. 257—258° (decomp.) (Found: N, 10·2. $C_{14}H_{12}O_3N_2$ requires N, 10·9%).

An alcoholic solution of the hydrazone is acid to litmus and gives a strong orange coloration with ferric chloride.

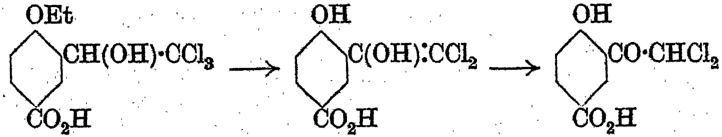
Oxidation of 5-Carboxy-2-ethoxyphenylglycollic Acid (IV) *to 2-Hydroxy-*1:5-iso*phthalic Acid* (V) *by Alkaline Potassium Permanganate.*—When the aqueous alkaline solution of the products of the action of potassium ethoxide upon anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene, obtained by diluting the mixture and distilling off the alcohol, was boiled and treated with a dilute aqueous solution of potassium permanganate until the colour of this was no longer discharged, a yellow solution was obtained. This was filtered from manganese dioxide, concentrated, and acidified with sulphuric acid. Ether then extracted 2-hydroxy-1:5-*iso*phthalic acid, from which the well-characterised ethyl ester was prepared.

The action of alcoholic potash upon the condensation product of *p*-hydroxybenzoic acid and chloral therefore takes place in the three stages (III ⟶ IV ⟶ V) shown on p. 687.

The action of alcoholic potash upon anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene is much less violent than its action upon the analogously constituted 5-nitro-compound, owing to the greater stability of the first product, 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene, which reacts with alcoholic potash sufficiently slowly to admit of its isolation as above described.

*Action of Sulphuric Acid upon 5-Carboxy-2-ethoxy-*1-βββ-*trichloro-α-hydroxyethylbenzene* (III) *and Formation of ωω-Dichloro-5-carboxy-2-hydroxyacetophenone* (VI).—A mixture of 10 g. of 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene and 100 c.c. of concentrated sulphuric acid was heated for 10 minutes on a water-bath; hydrogen chloride was then liberated. After cooling, the dark brown solution was poured into 500 c.c. of water, and the product, *ωω-dichloro-5-carboxy-2-hydroxyacetophenone*, which was mainly deposited as a colourless solid, was extracted with ether. On evaporation of the ether, a well-crystallised product was left which was moderately easily soluble in water and easily soluble in alcohol. It separated from a mixture of these solvents in thin, unctuous plates, m. p. 163—166°. When powdered, it is extremely irritating and causes violent sneezing (Found: C, 43·4; H, 2·7; Cl, 28·45. $C_9H_6O_4Cl_2$ requires C, 43·4; H, 2·4; Cl, 28·5%).

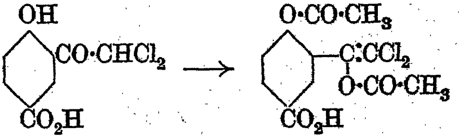
The compound must be formed by the elimination of hydrogen chloride under the influence of sulphuric acid followed by an intramolecular rearrangement thus:



ωω-Dichloro-5-carboxy-2-hydroxyacetophenone yields an *osazone* and a well-crystallised semicarbazone.

The osazone was obtained by gently boiling a slight excess of phenylhydrazine with a fairly concentrated alcoholic solution of the acetophenone. It separated as a yellow, crystalline mass and was recrystallised from boiling alcohol, in which it was moderately easily soluble, and from which it separated in canary-yellow needles, m. p. 243·5° (Found: N, 15·1. $C_{21}H_{18}O_3N_4$ requires N, 15·0%).

Acetyl Derivative of ωω-Dichloro-5-carboxy-2-hydroxyacetophenone.



—2 G. of the dichloro-acetophenone and 1 g. of anhydrous sodium acetate were added to 20 c.c. of acetic anhydride and heated gradually on an oil-bath. The liquid was allowed to boil gently for a few seconds, cooled, and poured into water; the viscid mass thus obtained was recrystallised from alcohol, from which it separated in colourless needles, m. p. 194—196° (Found: Cl, 21·5; C, 46·5; H, 3·1. $C_{13}H_{10}O_6Cl_2$ requires Cl, 21·3; C, 46·8; H, 3·0%).

Preparation of 5-Carboxy-2-hydroxyacetophenone, by Reduction of ωω-Dichloro-5-carboxy-2-hydroxyacetophenone (VI).—2 G. of ωω-dichloro-5-carboxy-2-hydroxyacetophenone and 25 c.c. of hydriodic acid (b. p. 126°) were heated to 115—120° for a short time. Reduction occurred very easily, free iodine was liberated, and on cooling the liquid *5-carboxy-2-hydroxyacetophenone* crystallised out. It was recrystallised from dilute alcohol, from which it separates in colourless, shining plates, m. p. 246—247° (Found: C, 59·9; H, 4·4. $C_9H_8O_4$ requires C, 60·0; H, 4·4%).

It is sparingly soluble in water and easily soluble in alcohol. Its aqueous solution gives a cherry-red coloration with ferric chloride.

It yields a well-characterised *phenylhydrazone* when its concentrated alcoholic solution is heated with a slight excess of phenylhydrazine. This is sparingly soluble in alcohol, from which it separates in long, pale-yellow needles, m. p. 286° (Found: N, 10·2. $C_{15}H_{14}O_3N_2$ requires N, 10·4%).

*The Action of Hydriodic Acid on 5-Carboxy-2-ethoxy-*1-βββ*-trichloro-α-hydroxyethylbenzene* (III).—2·7 G. of the substance were boiled gently for a short time with 25 c.c. of hydriodic acid (b. p. 126°). Iodine was liberated and, on cooling, 5-carboxy-2-hydroxyacetophenone crystallised out. After being recrystallised from dilute alcohol, it was obtained in shining plates, identical with those obtained by reduction of ωω-dichloro-5-carboxy-2-hydroxyacetophenone, and giving the same phenylhydrazone with phenylhydrazine.

In conclusion we desire to thank the "Real Academia de Ciencias" of Madrid and the Ramsay Memorial Fellowship Trust for the Fellowship awarded to one of us (F. C. P.) which enabled this work to be carried out.

THE QUEEN'S COLLEGE, OXFORD. [*Received, December 23rd*, 1926.]

CIV.—*The Mechanism of Reactions induced by Hydrogen Chloride between Aromatic Aldehydes and Aldehydecyanohydrins in Solution.*

By BERTRAM HOBART INGHAM.

THE object of this research was to elucidate the mechanism of the formation of oxazoles and other substances by the action of hydrogen chloride upon ethereal solutions of aromatic aldehydes and aldehydecyanohydrins. Fischer (*Ber.*, 1896, **29**, 205) first employed this method to prepare 2 : 5-diphenyloxazole, the constitution of which he established by an alternative synthesis and by degradation, but he made no suggestion as to the mode of formation of the final products.

The action of hydrogen chloride upon ethereal solutions (both dry and moist) of aldehydecyanohydrins, alone and also in the presence of aldehydes, has now been investigated, and, besides oxazoles, mandelamide derivatives and 3-keto-2 : 5-diaryl-3 : 4-dihydro-1 : 4-diazines have been obtained. The example studied in greatest detail was that of benzaldehyde and benzaldehydecyanohydrin (mandelonitrile), and the most salient observations made in connexion with this aldehyde and its derivatives may be summarised as follows :

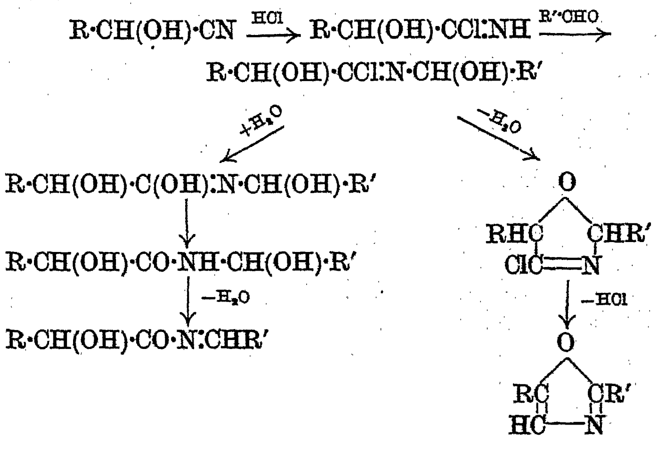
(1) Exclusion of moisture favoured oxazole formation and inhibited the production of mandeloarylideneamides, and *vice versa.*

(2) The " blocking " of the hydroxyl group of the cyanohydrin (*e.g.*, by benzoylation or by substitution of chlorine) precluded oxazole formation.

(3) Iminochlorides were produced as intermediates.

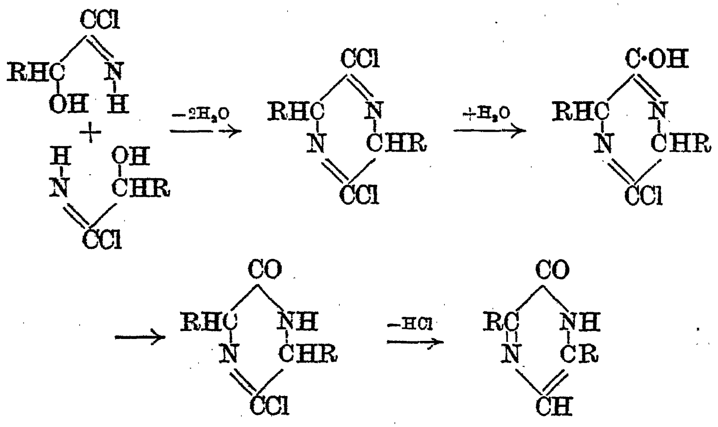
(4) The proportion of diazine derivative produced was greater in the absence than in the presence of free aldehyde.

The observations support the following mechanism for the production of oxazoles and mandeloarylideneamides from aldehydes and aldehydecyanohydrins :

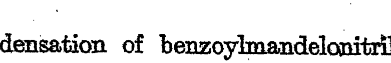


The diazine obtainable from benzaldehydecyanohydrin was first prepared from that substance by Minovici (*Ber.*, 1899, **32**, 2206), who, however, assigned to it an extremely improbable structure. Later, Japp and Knox (J., 1905, 87, 701) determined its constitution, but not its mode of formation. In this connexion, the generalisations (3) and (4) given above, and the statement of Japp and Knox (*loc. cit.*) that " . . . attempts to obtain the condensation product by acting on mandelonitrile with other dehydrating agents did not give the desired result . . ." are highly significant; they seem, however, to have been overlooked by previous workers. These observations support the following mechanism for the production of 3-keto-2 : 5-diaryl-3 : 4-dihydro-1 : 4-diazines from aromatic aldehydecyanohydrins :

$$\mathrm{R{\cdot}CH(OH){\cdot}CN} \xrightarrow{\mathrm{HCl}} \mathrm{R{\cdot}CH(OH){\cdot}CCl{:}NH}$$



Minovici also prepared a monobromo- and a mononitro-derivative of the diazine obtainable from benzaldehydecyanohydrin, and their formation is quite consistent with the structure assigned by Japp and Knox to this diazine if they are formulated thus :



$$\mathrm{OC}{<}\begin{matrix}\mathrm{NH{\cdot}CPh}\\\mathrm{CPh{=}N}\end{matrix}{>}\mathrm{CR}$$ (where R is Br or NO_2).

The condensation of benzoylmandelonitrile with benzaldehyde in ethereal solution in presence of hydrogen chloride gave no oxazole, but two isomeric forms of benzylidenebisbenzoylmandelamide. In the absence of benzaldehyde and moisture, the iminochloride of benzoylmandelonitrile was obtained, whilst if a trace of moisture was present benzoylmandelamide was produced. For similar reasons to those given for the production of oxazoles, the mechanism of the reactions would appear to be as follows :

$$\begin{tikzcd}
\mathrm{A{\cdot}CN} \arrow[r, "\mathrm{HCl}"] & \mathrm{A{\cdot}CCl{:}NH} \arrow[r, "\mathrm{H_2O}"] \arrow[d, "\mathrm{Ph{\cdot}CHO}"] & \mathrm{A{\cdot}C(OH){:}NH} \arrow[r] & \mathrm{A{\cdot}CO{\cdot}NH_2} \\
& \mathrm{A{\cdot}CCl{:}N{\cdot}CH(OH){\cdot}Ph} \arrow[r, "\mathrm{A{\cdot}CCl{:}NH}"] & \mathrm{[A{\cdot}CCl{:}N]_2CHPh} \arrow[d, "\mathrm{2H_2O}"] & \\
& \mathrm{[A{\cdot}CO{\cdot}NH]_2CHPh} & \mathrm{[A{\cdot}C(OH){:}N]_2CHPh} \arrow[l] &
\end{tikzcd}$$

$(A = \mathrm{CHPh{\cdot}OBz})$

EXPERIMENTAL.

General.—Hydrogen cyanide was prepared by Wade and Panting's method (J., 1898, **73**, 255), and redistilled over phosphorus pentoxide (except in experiments 1 and 2 of the benzaldehydecyanohydrin series). It was condensed with the aldehyde by being kept for at least 20 hours with this in ethereal (or ether–benzene) solution in the presence (except in the experiments 1 and 2 mentioned above) of tripropylamine as a basic catalyst (Ultée, *Rec. trav. chim.*, 1909, **28**, 718). The solvents required were dried with sodium and redistilled over phosphorus pentoxide, and the hydrogen chloride was dried with sulphuric acid and calcium chloride. The liquid aldehydes were redistilled several times in a vacuum, and the solid aldehydes (B.D.H.) were dried in a vacuum over concentrated sulphuric acid.

Condensation of Benzaldehydecyanohydrin and Benzaldehyde (compare Fischer, *loc. cit.*).—In each experiment benzaldehydecyanohydrin (12·5 g.; 1 mol.) and benzaldehyde (10 g.; 1 mol.) in 60 c.c. of dry ether were employed. After cyanohydrin formation had taken place (as described above), the solution, protected from moisture, was saturated at 0° with hydrogen chloride. The oxazole and mandelamide thus produced were separated by fractional crystallisation from alcohol and ligroin.

An ethereal solution of α-chlorophenylacetonitrile (see below) was saturated with hydrogen chloride, 1 mol. of benzaldehyde then added, and the passage of hydrogen chloride continued. An unidentified substance was obtained, but no 2 : 5-diphenyloxazole or mandelobenzylideneamide was detected in the product.

α-Chlorophenylacetonitrile was prepared by the action of thionyl chloride upon benzaldehydecyanohydrin in ethereal solution and obtained as a greenish-yellow, pungent liquid, b. p. 170°/ about 120 mm. It has an irritant action on the skin, and its vapour is a strong lachrymatory (compare Michaël and Jeanprêtre, *Ber.*, 1892, **25**, 1679).

Expt.	Special conditions of experiment.	Yields. 2 : 5-Diphenyloxazole hydrochloride. Grams.	%	Mandelobenzylideneamide. Grams.	%
1	As in (3), but without a solvent, with a drop of aqueous KOH as catalyst, and without exclusion of moisture...........	nil		nearly theoretical	
2	As in (3), but with 200 c.c. of solvent, and with catalyst as in (1)	trace		nearly theoretical.	
3	As outlined in the general description ...	14	58	7	31
4	As in (3); the cyanohydrin, however, was frozen in solid CO_2, and the highest-melting fraction (m. p. about 15°) employed *	10·5	43	8	36
5	As in (3), with addition of 7 g. of anhydrous zinc chloride	nil	—	15	67
6	As in (3), with addition of 15 g. of thionyl chloride immediately before passage of hydrogen chloride	9	37	nil ‡	—
7	As in (6), but with more rapid passage of hydrogen chloride.†	14	58	nil ‡	—

* Ultée (*loc. cit.*) gives the m. p. of pure benzaldehydecyanohydrin as 21·5—22°.

The relatively larger proportion of mandelobenzylideneamide obtained in this than in the previous experiment is explained by the assumption that the cyanohydrin absorbed a little atmospheric moisture during the process of freezing.

† The larger yield of oxazole hydrochloride in this case than in the previous one is in accordance with theoretical considerations—the condensation taking place more rapidly, the thionyl chloride would have less time in which to "block" the hydroxyl group of the cyanohydrin and thus prevent oxazole formation.

‡ A considerable quantity of α-chlorophenylacetonitrile was formed in each case.

Condensation of Benzoylmandelonitrile and Benzaldehyde.—By the action of hydrogen chloride upon an ethereal solution of benzoylmandelonitrile (Francis and Davis, J., 1909, 95, 1403) and benzaldehyde in molecular proportion, a white solid was produced, which was separated into two portions by extraction with alcohol for several hours. The residue, which was insoluble in acetone, acetic acid, and benzene, melted at 250—251° (Found: C, 74·0; H, 5·3; N, 5·1. $C_{37}H_{30}O_6N_2$ requires C, 74·2; H, 5·0; N, 4·7%); the sparingly soluble portion was an isomeride and crystallised from alcohol in microscopic needles, m. p. 223—224° (Found: C, 74·2; H, 5·5; N, 5·1%). 2 : 5-Diphenyloxazole could not be detected in the original alcoholic mother-liquor, even after concentration, by means of picric acid.

The two isomerides were readily debenzoylated by alcoholic potash, giving a substance which crystallised from alcohol in colourless, microscopic needles, m. p. 216—217° (Found: C, 70·4; H, 6·0; N, 7·7. $C_{23}H_{22}O_4N_2$ requires C, 70·8; H, 5·6; N, 7·2%). The isomerides were not affected by boiling dilute sulphuric acid, but when a solution of either in concentrated sulphuric acid was kept for ½ hour and poured into water, benzoic and mandelic acids, benzaldehyde and ammonia were formed. This reaction, in conjunction with the action of alcoholic potash upon the isomerides of m. p.'s 250—251° and 223—224°, shows that these substances are isomeric forms of *benzylidenebisbenzoylmandelamide*,

$$(OBz\cdot CHPh\cdot CO\cdot NH)_2CHPh.$$

This structure was confirmed by the isolation of a small quantity of the higher-melting isomeride (identity determined by the mixed melting-point method) from the product of the fusion of benzoylmandelamide (excess) and benzaldehyde at 140—160° for 2 hours.

The production of similar substances has been recorded—ethylidenedibenzamide (Hepp and Spiess, *Ber.*, 1876, **9**, 1425); benzylidenebisacetylmandelamide (Japp and Knox, *loc. cit.*).

Action of Hydrogen Chloride upon Benzoylmandelonitrile.—Hydrogen chloride, dried by sulphuric acid, was passed for about 20 hours through a dry, cooled, ethereal solution of benzoylmandelonitrile, protected from atmospheric moisture. On removal of the ether, a clear, viscous, amber-coloured oil remained which would not solidify, and gave benzoylmandelamide when boiled with 10% aqueous alcohol for 2 hours.

When moisture was not excluded during the reaction, much benzoylmandelamide was produced. After several crystallisations from alcohol, it was obtained as a colourless, microcrystalline mass, m. p. 160—161° (Found: C, 70·4; H, 5·8. Calc. for $C_{15}H_{13}O_3N$: C, 70·6; H, 5·1%) (compare Orton, J., 1901, **79**, 1354).

Condensation of Acetaldehydecyanohydrin and Benzaldehyde.—When these substances were condensed by hydrogen chloride in ethereal solution, lactobenzylideneamide, m. p. 132° (Found: C, 67·5; H, 6·5. Calc. for $C_{10}H_{11}O_2N$: C, 67·8; H, 6·2%), was formed, but no 2-phenyl-5-methyloxazole could be detected (compare Fischer, *loc. cit.*).

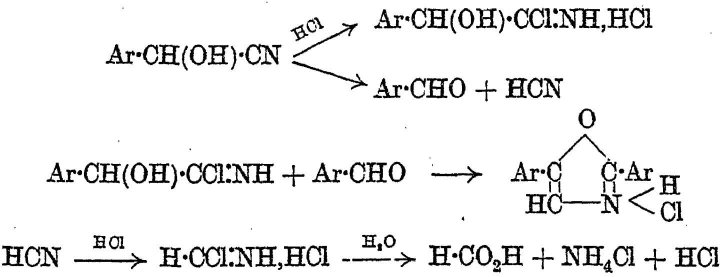
Condensation of Anisaldehydecyanohydrin and Anisaldehyde.—Minovici studied the action of hydrogen chloride upon anisaldehydecyanohydrin in ethereal solution alone (*Ber.*, 1899, **32**, 2206) and in the presence of anisaldehyde (*Ber.*, 1896, **29**, 2097) and obtained in each case a white, crystalline substance, $C_{17}H_{15}O_3N$, m. p. 145°. In the latter case he described it as 2 : 5-dianisyloxazole, but in the former he assigned to it the constitution $OMe\cdot C_6H_4\cdot CH(CN)\cdot CO\cdot C_6H_4\cdot OMe$

without giving any evidence for his conclusion. When his experiments were repeated, 2 : 5-dianisyloxazole, m. p. 143—144°, was isolated in each case (Found: C, 72·8; H, 5·6. Calc.: C, 72·6; H, 5·3%). The picrate was obtained in yellow needles, m. p. 214—216°, after one crystallisation from acetone.

Condensation of m-*Nitrobenzaldehydecyanohydrin and* m-*Nitrobenzaldehyde.*—This condensation was performed similarly to the preceding ones; it was necessary, however, to add some benzene to the ether to bring the aldehyde into solution. (Such addition was necessary in the succeeding condensations also.) The yellow reaction product was extracted for several hours with alcohol. The sparingly soluble substance (*A*) that separated from the extract was obtained as a canary-yellow, microcrystalline mass, m. p. 277—278°, after recrystallisation from glacial acetic acid (Found: C, 56·8; 56·8; H, 3·5, 3·6%). The residue from the extraction was separated by fractional crystallisation from acetic acid into a less soluble substance, m. p. 238° (Found: C, 57·9; H, 2·9. $C_{15}H_{9}O_{5}N_{3}$ requires C, 57·9; H, 2·9%), and a more soluble one, m. p. 225—227° (Found: C, 57·8; H, 3·2%). Since the latter remained unchanged in melting point after recrystallisation from acetic acid and from nitrobenzene, these two substances are regarded as isomeric forms of 2 : 5-*di*-m-*nitrophenyloxazole.*

Condensation of m-*Nitrobenzaldehydecyanohydrin and Benzaldehyde.*—The crude product contained a substance which, after four crystallisations from alcohol, was obtained in cream-coloured needles, m. p. 156—157°, and is probably 2-*phenyl*-5-m-*nitrophenyloxazole* (Found: C, 67·2; H, 3·9. $C_{15}H_{10}O_{3}N_{2}$ requires C, 67·7; H, 3·7%). A considerable quantity of the substance (*A*), m. p. 277—278° (see preceding experiment), was isolated from the crude product. That it is produced from the *m*-nitrobenzaldehydecyanohydrin only was proved by the following experiment.

Action of Hydrogen Chloride upon m-*Nitrobenzaldehydecyanohydrin.*—The action of hydrogen chloride upon an ether–benzene solution of this cyanohydrin produced a pale yellow substance which, when dried over paraffin wax and solid sodium hydroxide, contained ionic chlorine and melted at 95—99° (decomp.). When a methyl- or ethyl-alcoholic solution of it was kept or boiled, a precipitate formed rapidly. This precipitate, on purification, yielded a substance, m. p. 277—278°, identical with the substance (*A*), and much ammonium chloride and 2 : 5-di-*m*-nitrophenyloxazole were found in the mother-liquor. It seems probable, therefore, that the following reactions took place during the passage of hydrogen chloride into the cyanohydrin solution ($Ar = NO_2\cdot C_6H_4$),

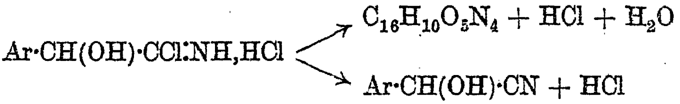


$$\mathrm{Ar{\cdot}CH(OH){\cdot}CN} \xrightarrow{\mathrm{HCl}} \mathrm{Ar{\cdot}CH(OH){\cdot}CCl{:}NH,HCl}$$

$$\mathrm{Ar{\cdot}CH(OH){\cdot}CN} \longrightarrow \mathrm{Ar{\cdot}CHO + HCN}$$

$$\mathrm{HCN} \xrightarrow{\mathrm{HCl}} \mathrm{H{\cdot}CCl{:}NH,HCl} \xrightarrow{\mathrm{H_2O}} \mathrm{H{\cdot}CO_2H + NH_4Cl + HCl}$$

and that on boiling the crude product with alcohol (or water) the following reactions occurred:



$$\mathrm{Ar{\cdot}CH(OH){\cdot}CCl{:}NH,HCl} \longrightarrow \mathrm{C_{16}H_{10}O_5N_4 + HCl + H_2O}$$

$$\mathrm{Ar{\cdot}CH(OH){\cdot}CCl{:}NH,HCl} \longrightarrow \mathrm{Ar{\cdot}CH(OH){\cdot}CN + HCl}$$

The similarity in the methods of preparation and in properties of the substance (*A*) and the compound obtained by Japp and Knox and by Minovici from benzaldehydecyanohydrin, makes it highly probable that they have similar structures. The substance (*A*) (Found: C, 56·8; H, 3·5. $C_{16}H_{10}O_5N_4$ requires C, 56·8; H, 3·0%) is therefore considered to be 3-*keto*-2 : 5-*di*-m-*nitrophenyl*-3 : 4-*dihydro*-1 : 4-*diazine*. Its colour is slowly changed from canary-yellow to moderately deep brown by light. When the diazine was treated with chromic and acetic acids, 80% of it was recovered unchanged and no trace of the remainder could be found.

Condensation of p-*Nitrobenzaldehydecyanohydrin and* p-*Nitrobenzaldehyde.*—This condensation was performed similarly to that of the *m*-isomeride, and 3-*keto*-2 : 5-*di*-p-*nitrophenyl*-3 : 4-*dihydro*-1 : 4-*diazine* was obtained as a canary-yellow, microcrystalline mass, m. p. 332—334° (Found: C, 56·9; H, 3·3. $C_{16}H_{10}O_5N_4$ requires C, 56·8; H, 3·0%), by extraction of the crude product twice with alcohol and crystallisation of the residue twice from acetic acid and once from nitrobenzene.

All the various residues were mixed together and, after removal of the solvents, the product was extracted several times with alcohol and finally crystallised from alcohol and from acetone, golden-yellow, microscopic needles of 2 : 5-*di*-p-*nitrophenyloxazole*, m. p. 228—232°, being obtained (Found: C, 58·4; H, 3·3. $C_{15}H_9O_5N_3$ requires C, 57·9; H, 2·9%).

Attempted Hydrolysis of "Minovici's Compound."—The compound was heated with concentrated hydrochloric acid (20 parts) in a sealed tube at 200° for 21 hours, and was converted thereby merely into its hydrochloride.

The author is indebted to Dr. H. Stephen for suggesting the subject of the research, and for valuable advice connected therewith, and also to the Chemical Society for a grant towards its cost.

THE UNIVERSITY, MANCHESTER. [*Received, January 20th*, 1927.]

CV.—*Studies in the Composition of Coal. The Resolution of Coal by Means of Solvents.*

By CHARLES COCKRAM and RICHARD VERNON WHEELER.

As the result of systematic researches initiated in 1912, which have followed since 1915 the scheme outlined by Stopes and Wheeler (*Rep. Brit. Assoc.*, 1916), we can now express the " analysis " of a coal in a form which indicates its properties more clearly than the usual " proximate " and " ultimate " analyses. For example, the characters of the four component bands of the Hamstead coal, a markedly banded bituminous coal, can be expressed in the following manner :

	Per cent. by weight.			
	Ulmin compounds.	Organised plant entities.	Hydrocarbons and resins.	General character of plant entities.
Vitrain	96	Nil.	4	—
Clarain	92	5	3	Cuticles and spore exines.
Durain	83	15	2	Cuticles, spore exines, and woody tissues.
Fusain	20	80	Nil.	Woody tissues.

In these analyses, certain resin-like compounds, which cannot be definitely classed as resins, present in the coals in small quantity, have been ignored.

Other researches have dealt, and are dealing, with the constitution of the ulmin compounds and the organised plant entities (see, *e.g.*, Tideswell and Wheeler, J., 1922, **121**, 2345; Legg and Wheeler, J., 1925, **127**, 1412; Francis and Wheeler, *ibid.*, p. 2236). The present research is concerned with that portion of a normal bituminous coal which can be extracted by organic solvents, the sometimes incorrectly named " resinous " portion.

In many bituminous coals there are inclusions of resinous matter, usually on the cleavage planes, which can be separated mechanically and are thus readily examined (see Wigginton, *Fuel*, 1926, **5**, 476). With these we are not at present concerned. The substances extractable from a normal bituminous coal by organic solvents presumably contain the remains of oils, fats, and waxes of the original coal-forming plants, in addition to resins and their degradation products disseminated throughout the coal mass, such as the microscopic rods preserved *in situ* in what are known to have been resin-containing cells (see White and Thiessen, *U.S. Bureau of Mines*, Bull. 38, 1913; Francis and Wheeler, J., 1926, 1410). All such substances, although they could not have formed more than a small proportion of the plants of coal-measure times, would yet, owing to their resistance to decay, survive and proportionately increase in amount while the plant material was accumulating and partly decaying in the early stages of coal formation.

Although this "resinous" portion forms but a small fraction of a bituminous coal, it is an important constituent technically, by reason of the properties it confers on the coal; and it is of considerable scientific interest in relation to the origin, mode of formation, and constitution of coal.

A critical survey of the more important work carried out before 1918 on the action of solvents on coal has been given by Stopes and Wheeler in their monograph "The Constitution of Coal" (London, 1918), reprinted, with additions by Dr. F. V. Tideswell bringing it up to date, in "Fuel in Science and Practice," Vol. III, 1924. Therein the value of pyridine, first suggested by Bedson (*Trans. Inst. Min. Eng.*, 1899, **16**, 388) as a means of resolving the coal conglomerate, was emphasised. Clark and Wheeler had found (J., 1913, **103**, 1704) that when the pyridine extract of a bituminous coal was treated with chloroform or benzene, up to 10% (on the original coal) dissolved. This fraction, soluble in both pyridine and chloroform, differed markedly in properties from the bulk of the coal, and from a consideration of those properties Clark and Wheeler concluded that their treatment had made "a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated" (*loc. cit.*, p. 1706). The portions of a bituminous coal (α), insoluble in pyridine, and (β), soluble in pyridine but insoluble in chloroform or benzene, were found to be of the same type, differing mainly in their behaviour towards pyridine, whilst both were quite distinct from (γ), the portion soluble in both pyridine and chloroform. Clark and Wheeler had termed the fractions (α) and (β) "cellulosic" or, alternatively, in conformity with a nomenclature used by Lewes (*J. Roy. Soc. Arts*, 1911, **60**, 135), "humic" compounds. Stopes and Wheeler (*loc. cit.*, p. 41) pointed out that, until the composition of these groups of compounds had been more definitely ascertained, it was desirable to use less dogmatic terms than "cellulosic" and "resinic," and proposed the non-committal labels α, β, and γ, which are now commonly used.

Jones and Wheeler (J., 1916, **109**, 707) summarised the information then available regarding the γ-compounds, which they considered to be derived mainly from the gums, resins, and starches of the original coal-forming plants. They are clearly a mixture of several classes of compounds. Jones and Wheeler (J., 1914, **105**, 140) had obtained from them, by the solvent action of pentane, crystals of paraffin wax (heptacosane), m. p. 55—59°, amounting to 0·10% on the original coal. We have now attempted further to resolve the mixture into simpler components by suitable solvents.

EXPERIMENTAL.

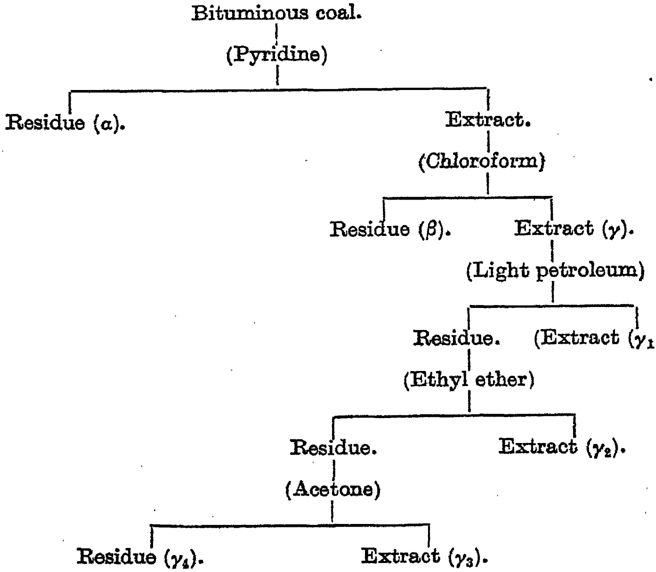
The γ-Compounds.—Supplies of the γ-compounds from the different coals were obtained by extraction with pyridine at its boiling point, followed by treatment of the extract with boiling chloroform. The action of pyridine on coal is often regarded as that of a reagent rather than a solvent. Harger (*J. Soc. Chem. Ind.*, 1914, **33**, 389) appears to have been the first to suggest that it effects "a process similar to depolymerisation." This view, for which no evidence has been adduced, has been adopted by later workers, notably by Illingworth ("Researches on the Constitution of Coal," London, 1921), but cogent reasons for rejecting it have been advanced by Tideswell (*Fuel*, 1922, **1**, 246). The work of Pearson (*J. Soc. Chem. Ind.*, 1923, **42**, 241) supports the view that pyridine is a solvent which resolves mechanically the colloidal mass of coal.

The first resolution of the coals in this research was by pure dry pyridine. The coals, dried and ground to pass a 10- and remain on a 60-mesh sieve, were extracted in large Soxhlet apparatus of special design. These and all subsequent extractions were carried out in an atmosphere of nitrogen. When extraction was complete, the solution was concentrated on a glycerol-bath and poured into a mixture of equal parts of concentrated hydrochloric acid and water. The mixed β- and γ-compounds were precipitated as a dark brown powder. This was filtered off, washed with dilute acid and with hot water, purified by steam distillation, and dried in a vacuum at 100°. In this way all but a trace of pyridine was removed.

The extraction of the γ-compounds by chloroform was completed in from 10 to 14 days. After removal of the solvent, the extracts were obtained as reddish-brown, brittle solids, m. p. 95—100°.

Resolution of the γ-Compounds.—In preliminary tests to determine the most suitable solvents with which to effect the resolution of the γ-compounds, acetone, ethyl ether, and light petroleum were found to be the most satisfactory. Ethyl alcohol tended to produce colloidal dispersion and therefore was not used.

With the particular sample of γ-compounds used in the preliminary experiments, acetone dissolved 85—90%, ethyl ether 70%, and light petroleum 33%. In the scheme of resolution finally adopted, the least effective solvent, light petroleum, was used first, the residue was extracted with ether, and any material then remaining was treated with acetone. The full scheme of resolution of the coals was as follows :



The fractions so obtained have distinctive properties, shortly to be described, which enable a judgment to be formed as to the character and origin of the groups of compounds each contains. We have made no attempt to isolate pure compounds, since a comprehensive research with this end in view is being carried out on a coal from Upper Silesia by Hofmann and Damm (see preliminary account, *Brennstoff-Chem.*, 1922, **3**, 73; 1923, **4**, 65).

In conformity with the nomenclature introduced by Stopes and Wheeler, the several fractions of the γ-compounds have been labelled, for convenience in reference, γ_1, γ_2, γ_3, and γ_4. A large number of bituminous coals have been resolved according to this scheme. In each instance the respective fractions have the same characteristics. It will therefore suffice here to record the results of examination by these means of one coal, a typical South Yorkshire coking coal from the Parkgate seam. This will be referred to as Parkgate A. The clarain portion only of the seam was examined. Its analysis is recorded in Table I.

By *treatment* with pyridine and chloroform, the proportions of α-, β-, and γ-compounds obtained were 75·8, 17·3, and 6·9%,

TABLE I.

Analysis of Parkgate A Clarain.

Proximate.		Ultimate.	
		Per cent. on ash-free, dry coal.	
Moisture	3·18%	Carbon	83·60
Ash	1·23%	Hydrogen	5·46
Per cent. on ash-free, dry coal.		Oxygen	6·75
Volatile matter, other than moisture	38·83	Nitrogen	1·72
"Fixed carbon"	61·17	Sulphur	2·47

respectively. Further resolution of the γ-compounds, in the manner described, gave the results recorded in Table II.

TABLE II.

Resolution of γ-Compounds. Parkgate A Clarain.

	% of total γ-compounds.	% of coal.	Ultimate analysis. C.	H.	S.	O + N.
Soluble in light petroleum (γ_1)	33	2·30	83·90%	9·00%	0·74%	6·36%
Soluble in ethyl ether (γ_2)	37	2·54	82·72	6·90	0·91	9·47
Soluble in acetone (γ_3)	12	0·83	79·00	5·70	0·89	14·41
Insoluble in acetone (γ_4)	18	1·23	80·00	5·90	1·10	13·00

The nitrogen contents of the fractions were not determined quantitatively, since minute traces of pyridine were sometimes retained by them. Each fraction could be completely redissolved in the cold solvent.

Examination of Fraction γ_1.—Extraction of the γ-compounds with light petroleum was completed in 14 days. The extract removed during the first few hours consisted entirely of hydrocarbons. As the extraction approached completion, the extract became darker in colour owing to the solution of some resinous matter. The total extract was a white, crystalline substance mixed with a certain amount of red oil. On drying in a vacuum, a reddish-brown material of the consistency of vaseline, mobile at temperatures above 80°, was obtained. On dissolving this material in ether and washing successively with dilute acid and alkali, traces of bases and fatty acids (volatile in steam) were obtained.

The remainder of the oxygenated compounds, forming 20% of the γ_1-fraction, were separated by Robinson's method (J., 1925, **127**, 768). They were resinous, dark red compounds, m. p. 90—95°, free from nitrogen and sulphur, completely soluble in cold chloroform, and of composition : C, 84·21 ; H, 7·31 ; O, 8·48%.

The rest of the γ_1-fraction consisted of saturated and unsaturated hydrocarbons in nearly equal amounts, and was similar to the neutral oils investigated by Hofmann and Damm (*loc. cit.*). The saturated hydrocarbons were obtained as a light yellow, faintly fluorescent oil having the characteristic odour of paraffins. Analysis gave: C, 87·4; H, 11·13; O, 1·47%, showing that hydrocarbons of other than straight- or branched-chain structure were present.

Fraction γ_1, 33% of the total γ-compounds, was thus found to consist of: Saturated hydrocarbons, 40; unsaturated hydrocarbons, 40; and resins, 20%.

Examination of Fraction γ_2.—The residue after the γ_1-compounds had been removed was a brown powder. This on extraction with ethyl ether (which was complete within 3 or 4 days) and evaporation of the solvent, yielded a brick-red powder, m. p. 100—110°. Small quantities of acids and pyridine bases were removed and the powdered extract was then shaken with a dilute solution of sodium bisulphite with a view to remove aldehydes and ketones. Neither of these groups of compounds was present.

Continuing the examination according to Tschirch's scheme for the separation of resin acids, the washed material was saponified in benzene solution with 10% alcoholic potassium hydroxide. A portion, 15% of the total fraction, dissolved, forming a dark red solution from which a light brown, flocculent powder was precipitated on acidification with hydrochloric acid; it was a mixture of phenols and acids (Found: C, 75·5; H, 5·9; O, 18·4%). These were separated by bubbling carbon dioxide through a sodium hydroxide solution of the mixture. There were thus obtained four fractions: *Precipitated by carbon dioxide*, (1) a brown solid; (2) a red oil extracted by ether. *Not precipitated by carbon dioxide*, (3) an oily acid volatile in steam; (4) a solid, non-volatile acid.

Fraction (1) formed 80—85% of the total saponifiable material. It consisted of a mixture of complex phenols soluble in hot alcohol, from which they were obtained on evaporation of the solvent as a brick-red powder (Found: C, 75·6; H, 6·3; O, 18·1%). Neither the mixture of the phenols themselves nor that of their benzoyl derivatives (which were brown powders) had a sharp m. p. Fraction (2) was a red oil having a powerful odour of limonene.

Fraction (3) was present in small quantity only. It was a volatile unsaturated acid. Fraction (4), 15·20%, was a mixture of acids from which insoluble silver, iron, and barium salts were obtained. Benzoyl chloride, both in pyridine and in aqueous alkaline solution, effected benzoylation. The acids were therefore hydroxy-acids.

The saponifiable portion of the γ_2-fraction thus consisted of phenols and hydroxy-acids in the form of esters, similar to the resin esters, or "resines" and "resinols," of Tschirch. The unsaponifiable portion was a dark red solid, m. p. 90—100°, free from nitrogen and sulphur (Found : C, 84·0; H, 7·2; O, 8·8%). In composition and general properties it closely resembled the resin separated from the γ_1-fraction. Tests showed that the oxygen it contained was not present in carboxylic, ketonic, aldehydic, or alcoholic grouping, but formed, presumably, a non-reactive bridged linkage. In its general inertness towards reagents, the substance was similar to the class of resins that Tschirch has termed "resenes."

Fraction γ_2, 37% of the total γ-compounds, was thus found to consist mainly of resins and resin-degradation products.

Examination of Fractions γ_3 *and* γ_4.—The residue from extraction with ethyl ether was a dark brown powder (m. p. 280—300° without decomp.). Acetone dissolved 40%, but the two fractions—γ_3, acetone-soluble, and γ_4, acetone-insoluble—were similar in composition (see Table II) and general properties. Both fractions were insoluble in alcoholic potassium hydroxide. Their resemblance to each other, and their dissimilarity from the γ_1 and γ_2 fractions, is best brought out by the results of destructive distillation and regulated oxidation, which will now be described.

Destructive Distillation of the Fractionated γ*-Compounds*.—One g. of each fraction was distilled in a small horizontal retort of Jena glass connected to an automatic Sprengel mercury pump. The retort was heated by an electric furnace, the temperature being raised slowly through intervals of 100° up to 450° and then of 50° to 600°. At each stage, the temperature was maintained constant until gases ceased to be evolved, a high vacuum being maintained, and the gases collected during each interval were analysed separately. The results are summarised in Table III.

TABLE III.

Destructive Distillation of Fractions of γ*-Compounds.*

A. Yields at 600°.

Fraction.	Total volatile matter, %.	Tar and oil, %.	Gas (c.c. per g.).
γ_1	(Distilled over unchanged below 300°.)		
γ_2	61·7	46·0	96·6
γ_3	48·3	13·0	140·5
γ_4	41·0	16·7	185·0

B. Gas analyses (%).

(Total gas over the range 15—600°.)

Fraction.	CO_2.	Higher olefines.	C_2H_4.	CO.	H_2.	Paraffins.
γ_2	5·2	2·0	1·0	6·5	32·5	54·4
γ_3	5·7	2·1	1·0	6·8	62·7	21·7
γ_4	6·2	2·3	1·7	9·5	52·0	28·2

The major portion of the tar from fraction γ_2 distilled between 200° and 300°. It consisted almost entirely of hydrocarbons. The residue was a dark brown, lustrous, intumescent mass, insoluble in chloroform. It will be seen that the gases evolved up to 600° contained a high proportion of paraffins.

The tars obtained from fractions γ_3 and γ_4 contained small quantities of phenols. The gases contained a high proportion of hydrogen and are thus dissimilar from the gases yielded by fraction γ_2. They more closely resemble the gases obtained from the β-fraction of the coal.

Oxidation of the Fractionated γ-Compounds.—Chemical analysis and the results of destructive distillation have thus shown the existence in the γ-compounds of three main types of constituents: hydrocarbons, resins, and a third group which has some of the characteristics both of resins and of coal-ulmins. The coal-ulmins, as exemplified by the β-compounds in particular, are readily oxidised, whereas the resins are not. We sought, therefore, to differentiate between the four γ-fractions by determining their relative ease of oxidation by hydrogen peroxide and dilute nitric acid.

Oxidation by hydrogen peroxide. One g. of each γ-fraction, as a fine powder, was treated under identical conditions with boiling hydrogen peroxide during 50 hours. The amount and character of the residues were then determined. The results are summarised in Table IV.

TABLE IV.

Oxidation of Fractionated γ-Compounds by Hydrogen Peroxide.

Fraction.	Residue, %.	Solubility of residue in KOH, %.	Analysis of residue.
γ_1	100	Nil.	
γ_2	90	Nil.	C, 78·1; H, 5·7; O, 16·2.
γ_3	Trace.	100	
γ_4	20	60	C, 70·8; H, 4·7; O, 24·5.

Fraction γ_1 was not affected by the treatment, but the more prolonged action of hydrogen peroxide removed the resinous material that this fraction contains, leaving hydrocarbons. Fraction γ_2 became lighter in colour and gradually lost its solubility in ether and in chloroform as it increased in oxygen content (compare Francis and Wheeler, J., 1925, **127**, 119). Fraction γ_3 reacted violently with each addition of hydrogen peroxide and was ultimately oxidised completely to water and oxides of carbon. Fraction γ_4 was not so reactive as γ_3, but was much more readily oxidised than γ_1 and γ_2. Much of the residue after oxidation was soluble in alkaline solutions, from which a brown, flocculent precipitate was obtained on acidification.

Oxidation by nitric acid. Since it was desired to avoid nitration, 30% nitric acid was used, 2·5 g. of the materials being boiled with 100 c.c. of the acid under reflux. Fraction γ_1 was not examined.

Fraction γ_2, which was rendered completely soluble in alkalis after 30 hours' treatment, showing that it contained no hydrocarbons, gave a copious evolution of nitrous fumes, and imparted a dark red colour to the nitric acid. The soluble acids (10%) did not contain picric acid. They were not further examined. The insoluble oxidation products (90%) were purified by washing with distilled water, dissolution in ammonia, and reprecipitation, as a reddish-brown powder, by dilute acid; further treatment with 30% nitric acid did not affect the composition (Found: C, 67·0; H, 4·6; O + N, 28·4%). The silver and copper salts of the acids were prepared and from combustion of the latter the equivalent was found to be 250.

Fractions γ_3 and γ_4 were treated together. The treatment, which was completed sooner than with fraction γ_2 and was accompanied by much frothing, rendered them completely soluble in alkalis. It was noted that the acids soluble in 30% nitric acid (10%) did not contain picric acid, but no further examination of them was made. The insoluble acids contained C, 60·9; H, 3·9; O + N, 35·2%, the composition remaining unchanged after further treatment with 30% nitric acid (Found: equiv., by combustion of copper salt, 268). As with similar products from fraction γ_2, benzene polycarboxylic acids were absent.

Whilst oxidation by hydrogen peroxide disclosed a difference in character between the γ_2- and the γ_3- and γ_4-fractions, oxidation by nitric acid shows a resemblance between all three fractions and a dissimilarity from coal-ulmins, such as the β-compounds from the same coal, which are rendered completely soluble in 30% nitric acid by prolonged treatment and yield both picric acid and benzene polycarboxylic acids (Francis and Wheeler, J., 1925, **127**, 2245).

We are in some doubt as to how the γ_3- and γ_4-fractions should be classed. The main bulk of any bituminous coal consists of groups of ulmin compounds, differing from each other according to the degree of condensation and dehydration they have experienced and differing, in consequence, as regards the extent to which they undergo colloidal dispersion in organic liquids. Just as the α-compounds are not dispersed in pyridine (whilst the β-compounds are), the β-compounds are not dispersed in chloroform; and it seemed possible that the γ_3- and γ_4-fractions might be ulmins that had been colloidally dispersed in chloroform.

In support of this suggestion, their low yield of tar and high yield of hydrogen on distillation in a vacuum, and their ease of oxidation by hydrogen peroxide, all relate them to the β-compounds. On the other hand, they melt, without decomposition, at temperatures no higher than do many resin inclusions from bituminous coals. No ulmins that we have examined, whether synthetic or of natural occurrence, melt on heating—all decompose without fusing. Moreover, their presumed dispersion in chloroform (no ulmin compounds are soluble in chloroform) indicates that they have undergone less change during the coalification process than the β-compounds. They should therefore be more readily oxidised. They are not; and, moreover, their products of oxidation by nitric acid are such as are yielded by resins rather than by ulmins.

On the whole, we consider the γ_3- and γ_4-fractions to be more nearly akin to the resins, representing perhaps the degradation products of some intermediate stage in the production of resins in the plant metabolism, such as gives rise to, *e.g.*, the tannins.

We therefore specify the various fractions of the γ-compounds from a bituminous coal as follows:

γ_1 (soluble in light petroleum): Mainly hydrocarbons. In the example described, some 20% of resins were also present.

γ_2 (soluble in ethyl ether): Resinols, resines, and resenes.

γ_3 and γ_4 (insoluble in ethyl ether): Resin-like.

It may here be noted that the resins which occur macroscopically in bituminous coals are rarely of the same degree of solubility as modern resins, and the usual resin solvents, such as ether, alcohol, and benzene, do not dissolve them completely.

We have been surprised not to obtain direct evidence, in any of the coals that we have examined, of the presence of waxes (esters of fatty acids and alcohols). In the cuticles of modern plants, waxes invariably coat or permeate the cutin layer, whilst the cuticles that form so large a proportion of the Russian papierkohle have about 4% of wax associated with them (Legg and Wheeler, Safety in Mines Research Board Paper No. 17, 1925). Such waxes are particularly resistant to bacterial decay and one would expect them therefore to accumulate in the coal-forming deposits. The explanation of their absence is probably to be found in the behaviour of the montan wax of brown coals on being heated. Montan wax is a mixture of resins with carboceric and montan acids ($C_{27}H_{54}O_2$) both free and esterified with tetracosanol and ceryl and myricyl alcohols. The wax does not contain free hydrocarbons in any quantity, but it begins to decompose at about 200°, yielding solid and liquid hydrocarbons (Schneider and Tropsch, *Ges. Abh. Kennt. Kohle*, 1917, **11**, 28). It may be, therefore, that a portion of the free hydrocarbons found in bituminous coals (fraction γ_1) represents the waxes originally present.

As examples of the fractionation of the γ-compounds of other coals, we may record the following (Table V). The coals are arranged in order of their carbon contents, the results obtained with Parkgate A being included for comparison.

TABLE V.

Fractionation of γ-Compounds.

(Percentages on ash-free, dry coal.)

	γ_1.	γ_2.	γ_3.
1. Vermilion County, Illinois, U.S.A. C, 76·7; H, 5·8.	2·13 (C, 86·0; H, 9·2.)	2·67 (C, 79·8; H, 6·3.)	1·20 (C, 80·3; H, 6·3.)
2.* Ayr Hard. C, 78·5; H, 5·9.	1·92	2·43	2·92
3.† Hamstead, Staffs. C, 79·3; H, 5·3.	1·06 (C, 85·9; H, 9·4.)	2·95 (C, 80·6; H, 6·5.)	0·98 (C, 79·7; H, 5·5.)
4.* Blackband. C, 79·5; H, 5·5.	2·37	2·85	2·28
5.* Top Hard. C, 80·1; H, 5·5.	1·61	2·40	2·62
6.† Wigan Six Feet. C, 82·0; H, 5·5.	2·92	1·57	3·67
7.† Parkgate B1, S. Yorks. C, 83·4; H, 5·5.	1·50 (C, 86·1; H, 9·3.)	1·75 (C, 84·0; H, 6·4.)	1·75
Parkgate B2, S. Yorks. C, 83·2; H, 5·8.	1·60 (C, 86·2; H, 9·2.)	4·20 (C, 84·0; H, 6·7.)	1·40 (C, 80·2; H, 5·9.)
8.† Ten Feet, Staffs. C, 83·4; H, 5·4.	2·30	2·16	4·34
9.† Parkgate A, S. Yorks. C, 83·6; H, 5·4.	2·30 (C, 83·9; H, 9·0.)	2·54 (C, 82·7; H, 6·9.)	2·06 (C, 79·5; H, 5·8.)
10.† Silkstone, S. Yorks. C, 83·6; H, 5·4.	2·26	1·52	5·14
11.† Arley, Lancs. C, 84·3; H, 5·4.	1·52	2·30	5·18
12.† Busty (Tudhoe), Durham. C, 85·1; H, 5·4.	1·72 (C, 88·4; H, 9·0.)	2·59 (C, 86·1; H, 6·5.)	3·68 (C, 84·4; H, 5·7.)
13.† Busty (Beamish Mary), Durham. C, 87·8; H, 5·4.	1·35	1·56	5·91

* Durain portion. † Clarain portion. The Hamstead clarain contained a high proportion of vitrain streaks.

The Parkgate samples B1 and B2 (No. 7 in Table V) are of particular interest. They were chosen from a section of the seam taken about 12 miles from Parkgate A, as representing the upper and lower clarain bands in that seam. This seam is a good example of a banded coal in which the several bands are of considerable thickness and can be mined separately. Since the several bands have distinctive properties, this is often desirable. The seam is characterised throughout the S. Yorkshire coal-field by the existence of a broad (1—2 ft.) central durain band with equally broad clarain bands above and below it (see Evans, " The Correlation of the Parkgate Seam," *Trans. Inst. Min. Eng.*, 1926, **71**, 451). The lower clarain band in this section differs from the upper in containing many bright bands in which, under the microscope, resin rods can be distinguished amongst the woody structures. Their presence has markedly increased the proportion of fraction γ_2 extractable from the coal. It is perhaps necessary to point out that, in records of a study of the chemical constitution of a banded bituminous coal, the character of the band investigated should be specified.

It was at one time held that a certain proportion of γ-compounds in a coal was essential if a good commercial coke was to be made from it (Illingworth, *J. Soc. Chem. Ind.*, 1920, **39**, 133T). This is probably true, in general, but it has long been realised that a measure of the quality of the coke that could be obtained from a coal was not given by its content of γ-compounds. This is not surprising in view of the varying proportion in which the several fractions, each having different characteristics, are present in the γ-compounds of different coals, as shown in Table V. The determination of the effectiveness of the several γ-fractions in causing the agglutination of the remainder of the coal during the process of coking throws considerable light on their properties. Coking tests were made on blends of the coal residues, left after extraction, with each one in turn of the γ-fractions from the same coal, in the proportions in which they originally existed. The blends were made by dissolving the extracts in chloroform and immersing the residues in the solutions. After being allowed to soak during several hours, the solvent was removed by evaporation in a vacuum. Throughout the operations, care was taken to avoid oxidation of any of the ingredients of the blends, since oxidation of any one of them adversely affects the quality of the coke yielded (compare Parr and Hadley, *Univ. Illinois Bull.*, 76, 1914). The test employed was that commonly used when attempting to assess the coking-value of a coal, *viz.*, the standard crucible test for the determination of " volatile matter " (" Interim Report on Methods of Analysis of Coal, 1923," Fuel Research Board, Survey Paper No. 2, H.M. Stationery Office). As an example of the results, we may quote those obtained when the coal used for the tests was Parkgate A clarain, which gives a good quality coke in practice. The following observations were made :

A blend of the separated α-, β-, and γ-compounds, in the proportions in which they were obtained from the coal, gave a hard, well-sintered coke-button of nearly the same character as did a sample of the original coal, showing that the α- and β-compounds had not suffered any material change during their separation.

A blend of the α- and β-compounds with only the γ_1-fraction gave in most of the tests a hard, well-sintered coke-button. A rather friable residue was occasionally obtained, which may be attributed to the fact that it is difficult to obtain satisfactory admixture of the extracted coal and this oily extract—there is a tendency for the extract to remain on the surface of the coal and to be volatilised during the coking test before it has been able to exert its agglutinating action. All such tests necessarily suffer from the fact that they do not reproduce exactly the original conditions of existence of the extracted material within the coal substance.

A blend of the α- and β-compounds with the γ_2-fraction gave a hard, well-sintered, and slightly swollen coke-button.

A blend of the α- and β-compounds with either the γ_3- or the γ_4-fraction gave a barely coherent residue, easily powdered between the fingers.

A discussion of the conditions necessary for the production of a good commercial coke would be out of place in this journal, but it may be said that, with regard to the composition of the coal, success does not rest solely on the use of a coal containing a sufficiency of some " coking principle." In so far as the presence of a " coking principle " is necessary, the conclusion can be drawn from this research that the agglutinating medium during coke-formation consists of the resins and hydrocarbons contained in the coal or is yielded by those resins and hydrocarbons during the early stages of heating in the coke-oven.

The Treatment of Bituminous Coals with Benzene.

Under atmospheric pressure, boiling benzene removes very little from most bituminous coals, but under higher pressures it apparently dissolves more. The most important researches in which this method of treating coal has been employed are those of Fischer, Broche, and Strauch (*Brennstoff-Chem.*, 1924, 5, 299; 1925, 6, 33), following preliminary experiments of Fischer and Gluud (*Ges. Abh. Kennt. Kohle*, 1916, 1, 54), who found that at a pressure of 50 atms. (b. p. of benzene about 288°), a bituminous coal yielded, after several treatments, as much as 6·7% of extract.

Fischer, Broche, and Strauch have indicated an important relationship between the character of the substances extractable by benzene under pressure and that of the coal treated, which may throw light on the character of the coalification process. Briefly, they suggest that their work shows that with increasing geological age of the coals the ratio of free hydrocarbons to resins increases, whilst the decomposition temperatures of the resins are raised.

We considered it important to institute a comparison between the substances obtained by resolving a coal with pyridine and chloroform and what may be termed "pressure-benzene" extracts such as those described by Fischer, Broche, and Strauch. We therefore carried out experiments on a number of bituminous coals in a similar manner. As a preliminary, we wished to know the effect, if any, of preheating a bituminous coal in an inert atmosphere at 250—280° on the amount of extractable matter it would subsequently yield to benzene or chloroform in the cold, Harger (*loc. cit.*) having stated that preheating at as low a temperature as 200° has the effect of greatly increasing the amount soluble in chloroform. We therefore sought this information from Mr. H. Berry, of the staff of the Fuel Research Board, who has been carrying out such experiments, and we have the permission of the Director of Fuel Research to quote some of his results (see Table VI).

TABLE VI.

The Effect of Preheating Bituminous Coal on its Solubility in Chloroform and Benzene. (H. BERRY.)

Extractable matter (% on ash-free, dry coal).

Coal.	Parkgate Brights.*		Parkgate Hards.†		Barnsley Brights.*		Barnsley Hards.†	
Solvent.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.	$CHCl_3$.	C_6H_6.
Without preheating.	1·45	0·37	1·39	0·50	0·73	0·31	1·15	0·59
After preheating at 200°	1·01	0·41	1·56	0·73	0·86	0·15	1·45	0·53
After preheating at 250°	2·75	0·54	2·72	0·71	1·20	0·30	2·37	0·34
After preheating at 350°	5·88	1·35	4·63	1·61	5·15	0·68	4·44	1·27

* *I.e.*, clarain and vitrain. † *I.e.*, durain.

It would thus seem that a change in a bituminous coal, which may be decomposition of some ingredient, is effected by heating at temperatures higher than 200°. In the work on the coking power of coal by Fischer, Broche, and Strauch (who were well aware of this effect of preheating), its incipient decomposition was of little moment, but we were anxious to remove the extractable matter unchanged, for comparison with the γ-compounds. Our first pressure-benzene extractions were therefore made at 200°.

The coals were ground to pass a 10- and remain on a 40-mesh sieve, and were dried in a vacuum. The extractions were carried out in an autoclave in an atmosphere of nitrogen, 4 or 5 successive treatments of each coal with pure benzene being made. After removal of the benzene, the extracts were obtained as dark brown, viscous solids. The following results, obtained with Parkgate A clarain, can be regarded as typical.

Treatment of Parkgate A Clarain with Benzene.—(*a*) *At* 200°. The extract amounted to 5·96% of the coal. This was fractionated according to the scheme adopted for the γ-compounds, and yielded :

	% of coal.
Soluble in light petroleum.	2·22 (C, 85·0; H, 9·0.)
Soluble in ethyl ether.	2·02 (C, 84·0; H, 6·8.)
Insoluble in ethyl ether.	1·72 (C, 82·5; H, 5·95.)

In physical character and general chemical properties the substances were similar to the corresponding fractions of the γ-compounds.

These results should be compared with those recorded in Table II, from which it will be seen that the pressure-benzene extraction at 200° has removed all the hydrocarbons but has left a proportion of the resins and resin-like substances undissolved. These were removed from the coal residue in the autoclave by extracting it in a Soxhlet apparatus with pyridine and treating the extract with chloroform, 1·1% of soluble material being obtained. This was partly soluble in ethyl ether, the proportions, expressed as percentages on the original coal, being: ether-soluble, 0·66 (C, 82·0; H, 6·8%), and ether-insoluble, 0·44 (C, 80·0; H, 6·2%). The total amount extracted from the Parkgate A clarain by treatment with benzene at 200°, followed by resolution with pyridine and chloroform, was thus 7·06%, a figure which compares closely with the percentage of γ-compounds (6·9) obtained from this coal by direct resolution with pyridine and chloroform.

(*b*) *At* 285°. In order to compare our results more closely with those of Fischer, Broche, and Strauch, we now extracted a sample of the same coal with benzene at 285°, using 6 successive treatments in the autoclave. The extract amounted to 7·3% on the ash-free, dry coal. It was fractionated with light petroleum and ether and yielded (per cent. on the original coal): soluble in light petroleum, 2·55 (C, 85·4; H, 9·2); soluble in ether, 1·97 (C, 84·2; H, 7·3); insoluble in ether, 2·78 (C, 79·4; H, 5·8). Resolution of the residual coal from the autoclave with pyridine and chloroform yielded a small quantity of material (about 0·7% on the coal) completely soluble in ether.

The higher temperature of extraction thus appears to have caused decomposition of part of the resins, with the result that the proportions of hydrocarbons and resin-like material insoluble in ether have been increased. Some other part of the coal-substance also seems to have been decomposed. A direct comparison of the different fractionations (Table VII) will make this clear.

TABLE VII.

	Resolution by pyridine and chloroform.	Pressure-benzene extraction.	
		at 200°.	at 285°.
Soluble in light petroleum (hydrocarbons).	2·30* (C, 83·9; H, 9·0.)	2·22 (C, 85·0; H, 9·0.)	2·55 (C, 85·4; H, 9·2.)
Soluble in ethyl ether (resins).	2·54 (C, 82·7; H, 6·9.)	2·02† (C, 84·0; H, 6·8.)	1·97† (C, 84·2; H, 7·3.)
Insoluble in ethyl ether (resin-like substances).	2·06 (C, 79·5; H, 5·8.)	1·72‡ (C, 82·5; H, 5·6.)	2·78 (C, 79·4; H, 5·8.)
Total.	6·90	5·96	7·30

* Contains 20% of resins, owing to prolonged Soxhlet extraction.

† On adding the ether-soluble fractions (0·66 and 0·7%, respectively) obtained on resolving the residue from the autoclave with pyridine and chloroform, these figures become 2·68 and 2·67%, respectively.

‡ On adding the ether-insoluble fraction (0·44%) obtained on resolving the residue from the autoclave with pyridine and chloroform, this figure becomes 2·16.

The method used by Fischer, Broche, and Strauch to fractionate their pressure-benzene extracts was to pour them into light petroleum, causing separation of insoluble solids, which they termed *Festbitumen*. On filtering these off and evaporating the light petroleum, viscous oils (*Ölbitumen*) were obtained. From our results it will be realised that this method effected a separation of the hydrocarbons from the resins and the resin-like compounds, probably a better separation than in our experiments, since our prolonged extraction with light petroleum in a Soxhlet apparatus dissolved some of the resins. Particular interest therefore attaches to their deduction that the former increase in amount, at the expense of the latter, with the geological age of the coal. The principal data on which this deduction is founded are recorded in Table VIII.

In conformity with the higher proportions of hydrocarbons removable from the older coals, their pressure-benzene extracts as a whole were more mobile, the most mobile being that obtained from a Ruhr anthracite (not included in Table VIII). The results certainly suggest a gradual increase in the proportion of hydrocarbons contained in the coal as the process of coalification proceeds, if it is considered that no thermal decomposition has occurred at the high temperature of extraction employed. We can make no statement on this point regarding the German coals, but we can affirm that with all the British coals we have tested appreciable decomposition takes place, hydrocarbons being produced at the expense of resins (see, *e.g.*, Table VII). Apart from this disadvantage, we cannot

TABLE VIII.

Treatment of Different Coals with Benzene at 285°.

(Fischer, Broche, and Strauch.)

Description of coal.	Percentages on ash-free, dry coal.		
	Total extract.	Hydrocarbons (Ölbitumen).	Resins and resin-like compounds (Festbitumen).
Dilsburg, Saar. C, 74·3; H, 5·3.	1·98 (C, 84·5; H, 7·9.)	1·04 (C, 89·3; H, 9·6.)	0·94 (C, 87·0; H, 6·5.)
Lohberg, Ruhr. C, 79·3; H, 5·6.	4·60 (C, 87·6; H, 7·0.)	2·48	2·12
Altenwald, Saar. C, 85·5; H, 6·7.	4·56 (C, 86·3; H, 6·7.)	2·55	2·01
Dudweiler, Saar. C, 86·5; H, 5·2.	7·76 (C, 87·9; H, 6·7.)	5·10	2·66
Prosper, Ruhr. C, 88·3; H, 5·2.	7·45 (C, 91·3; H, 6·9.)	(Not determined.)	
Osterfeld, Ruhr. C, 89·5; H, 5·8.	5·0 (C, 91·6; H, 6·9.)	3·40	1·60
Thyssen, Ruhr. C, 90·3; H, 5·4.	7·60 (C, 88·5; H, 6·7.)	5·10 (C, 92·2; H, 7·2.)	2·50 (C, 89·6; H, 6·1.)

regard pressure-benzene extraction as a satisfactory method of resolving British bituminous coals, for it does not appear to be equally effective with all. For example, the Hamstead clarain, which was found to contain 5·0% of γ-compounds on resolution with pyridine and chloroform, only yielded 1·6% of extractable matter to benzene at 200° and 4·5% at 285°. At the latter temperature, marked thermal decomposition took place.

Fischer, Broche, and Strauch's method of pressure-benzene extraction has been employed for several coals by Bone, Pearson, and Quarendon (*Proc. Roy. Soc.*, 1924, *A*, **105**, 608). Having poured the benzene extract into light petroleum, the last-named authors fractionated the *Ölbitumen* with benzene-free light petroleum and the *Festbitumen* with ethyl alcohol, thus obtaining four portions which they describe as follows: " (I) A yellowish-brown, non-nitrogenous portion soluble in light petroleum. (II) A nitrogenous reddish-brown solid, of low softening point, soluble in a mixture of 4 parts of light petroleum and 1 part of benzene. (III) A non-nitrogenous resinous portion. (IV) A group of nitrogenous bodies of ' humic ' type " (*loc. cit.*, p. 613).

The main reason for describing fraction IV as " humic " (a synonym for ulmic) appears to have been that it contained 1·1—1·5% of nitrogen. Be that as it may, this fraction should correspond with our γ_3- and γ_4-fractions, if ethyl alcohol were an effective solvent for coal-resins. In our experience, this seemed doubtful. We therefore subjected pressure-benzene extracts of the Parkgate A clarain to fractionation according to a variant of Bone, Pearson, and Quarendon's scheme, with the following results :

Extraction with Benzene.—(*a*) *At* 200°. Total extract, 6·00. Soluble on pouring into light petroleum, 2·00; soluble in ethyl alcohol, 0·90; insoluble in ethyl alcohol, 3·10, all as % on the ash-free, dry coal. The alcohol-soluble fraction was similar in character to the ether-soluble fraction obtained from the pressure-benzene extract at 200° previously described, but was less in quantity (see Table VII). The fraction insoluble in ethyl alcohol was now extracted with ethyl ether, resins amounting to 1·4% of the coal dissolving.

(*b*) *At* 285°. Total extract, 7·29. Soluble on pouring into light petroleum, 2·30; soluble in ethyl alcohol, 1·00; insoluble in ethyl alcohol, 3·99, all as % on the ash-free, dry coal. On extracting the alcohol-insoluble material with ether, resins amounting to 1·22% of the coal dissolved.

These results are summarised in Table IX and should be compared with those given in Table VII.

TABLE IX.

Fractionation of Pressure-Benzene Extracts of Parkgate A Clarain.

(% of ash-free, dry coal).

	Extracted at 200°.		Extracted at 285°.	
Soluble in light petroleum.	2·00 (C, 86·2; H, 9·1.)		2·30 (C, 85·9; H, 9·4.)	
Soluble in ethyl alcohol.	0·90 (C, 83·2; H, 6·75.)	2·30	1·00 (C, 83·4; H, 6·8.)	2·22
Soluble in ethyl ether.	1·40 (C, 84·5; H, 6·9.)		1·22 (C, 84·5; H, 7·2.)	
Insoluble.	1·70 (C, 82·6; H, 6·0.)		2·77 (C, 80·1; H, 5·9.)	

The fraction of the Parkgate A clarain which would be described by Bone, Pearson, and Quarendon as "humic" (fraction IV) thus contained about 30—45% of resins; the remainder was what we have termed resin-like.

The research of Bone, Pearson, and Quarendon, like that of Fischer, Broche, and Strauch, deals with the probable importance of the various fractions of the pressure-benzene extracts as regards the coking power of the coals containing them. We propose to discuss this subject in detail in a communication to a technical journal, but may here note that Bone, Pearson, and Quarendon correlate the coking power of a coal with its content of that portion of the pressure-benzene extract (at about 285°) insoluble in light petroleum and ethyl alcohol (their " Fraction IV "). We have shown that this fraction (in the coals that we have examined) consists of two classes of compounds—resins, soluble in ethyl ether, and compounds, allied to the resins, insoluble in that solvent. " Fraction IV," from the Parkgate A clarain, contains about 30% of ether-soluble and 70% of ether-insoluble compounds, but in this material from other bituminous coals the proportions are different. Apart from general considerations regarding the coking process, into which we need not here enter, it is therefore difficult to attach value to an apparent relationship between the coking power of a coal and its content of such indefinite constituents (or, in part, products of thermal decomposition).

The observations of Fischer, Broche, and Strauch on the change in character of the substances extractable from a coal with its geological age, or degree of coalification, seem to us to require, and to merit, amplification. We have therefore undertaken an examination of a series of coals, from the same seam, of increasing carbon content, adopting the method of resolution described in the first portion of this paper.

Much of the information contained in this paper was obtained during the course of an investigation that we are carrying out for the Safety in Mines Research Board, to whom we are indebted for permission to utilise it. Our thanks are also due to Mr. A. L. Godbert for a number of the data employed.

THE UNIVERSITY, SHEFFIELD. [*Received, October* 15*th*, 1926.]

CVI.—*The Constituents of the Cell-wall of the Flax Fibre.*

By ALBERT ERIC CASHMORE.

IN the past, investigations of the chemical constituents of the flax fibre dealt nearly always with materials, such as commercial raw fibre and yarn, in which non-fibrous tissues adhered to the fibre proper. This complex assemblage of tissues, comprising fragments of epidermis, cortex, soft-bast, and usually wood, contains a large variety of substances, and although it is customary to refer to the flax fibre as a pectocellulose, there is little definite knowledge of the distribution of the pectic constituents among the various tissues present in the raw fibre. Moreover, the loss in weight suffered by linen materials in the preliminary treatments with boiling alkalis is generally attributed, on very insecure grounds, to the removal of pectic constituents. This assumption is based mainly on the evidence of Kolb (*Bull. Soc. Ind. Mulhouse*, June, 1868. See also Cross and Bevan's "Cellulose," 1918, p. 218), who states that pectic acid is precipitated when the spent alkaline lyes obtained in the kier-boiling of linen are acidified.

During the past few years our knowledge of the chemistry of pectin has been considerably enlarged (see, for example, Carre, *Ann. Bot.*, 1925, 811, where a summary of the literature dealing with the properties and constitution of pectin is given) and better methods have been devised for the extraction of pectin from plant tissues and for its estimation, either after extraction or *in situ.* Honneyman (*J. Text. Inst.*, 1925, **16**, 370T) has recently carried out estimations of pectin in commercial flax fibre, using the method of Ling, Nanji, and Paton (*J. Soc. Chem. Ind.*, 1925, **44**, 253T), and has shown that the pectic content of the retted fibre is very low (some 4—6%), whereas by the action of boiling dilute alkalis the fibre loses some 25% in weight. Similar results have been obtained in unpublished work carried out in these laboratories, and it has been shown that the fibres, freed from extraneous tissues by treatment with a hot soap solution as described later, contain less than 1% of pectin.

Reference may be made at this point to a paper by Schmidt, Haag, and Sperling (*Ber.*, 1925, **58**, 1394) on the so-called incrusting substances of flax. The authors do not state definitely the nature of the material used, but presumably it was the retted and scutched fibre of commerce. By successive treatments of the material with solutions of chlorine dioxide and sodium sulphite, a separation of the "incrusting" substances was effected, leaving the "skeletal" substances. In this way, the following figures were obtained:

Skeletal substances	49·9% (wt. of ash deducted).
Incrusting substances	38·9% (wt. of ash deducted).
Moisture content	7·7%.

The skeletal substances so obtained contained 3·8% of a hemicellulose soluble in cold 5% sodium hydroxide solution, and when this was removed the residual "cellulose" still contained 5% of "pentosan." The cellulose content of the fibre thus indicated is only about 40%, and it is clear that the "incrusting substances" of these authors include the bulk of the non-cellulosic constituents of the fibre wall with which we are concerned in this communication. There is, however, no evidence as to which of the constituents examined by them came from the fibre-strands and which from the adherent tissues.

In a paper entitled "The Incrustations of Flax," Ehrlich and Schmidt (*Biochem. Z.*, 1926, **169**, 13) describe the substances obtained by the extraction of flax straw with water at temperatures varying from 50° to 130°, but in this case also no evidence was given to show from which tissues the substances examined were derived.

The fibre employed in the present investigation was obtained from unretted flax straw of good quality, pulled at about the customary stage of ripeness. This was broken and scutched without retting, and after hand-combing to remove the bulk of the adherent shives, was extracted with a hot soap solution. In this way, the remaining adherent tissues were loosened from the fibre-strands, and, as microscopic examination showed, could be completely removed by careful washing. The adherent tissues could not be readily removed from retted fibre by this treatment. It was found that the unretted fibre-strands cleaned by the soap treatment lost practically nothing in weight when placed for several days in a retting tank containing actively retting flax straw. It may be concluded, therefore, that the fibre-strands from unretted straw, purified as described, contained no appreciable amount of substances which are normally removed in retting. In order to remove small quantities of waxy and resinous constituents, the fibre-strands were next extracted with a mixture of ethyl alcohol and benzene. The small remaining quantity of pectin was then removed by the prolonged action of a hot dilute solution of ammonium oxalate. Finally, the fibre was leached with a cold 4% solution of sodium hydroxide, in order to remove free hemicelluloses.

The fibre-strands, after such purification, still contain some 15—16% of substances which may be removed by the action of boiling dilute alkalis, such as 2% sodium hydroxide or barium hydroxide solution. The nature of these alkali-soluble constituents and their mode of attachment to the cellulose form the main subjects of this communication. Since the soap-cleaned fibre-strands contain no adherent tissues, and also since the middle lamella between the fibre cells clearly represents only a very small proportion by weight of the material, it may be concluded that the bulk of the alkali-soluble substances is associated with the cellulose of the cell-wall. The association of cellulose and alkali-soluble substances in the fibre-strands, purified by the method described, will be referred to as the *cellulose-complex.*

This cellulose-complex was found by Cross and Bevan's method to contain 88·5% of " total cellulose " and 76·5% of " α-cellulose." Since the loss in weight produced by the action of boiling dilute sodium hydroxide solution on the cellulose-complex amounted to some 16%, it would appear that the " total cellulose " estimated by Cross and Bevan's method must include some of the alkali-soluble constituents of the fibre, and that the substances removed by the 17·5% solution of sodium hydroxide (employed in the α-cellulose estimation) must include all the alkali-soluble constituents. For the estimation of the cellulose content of the cellulose-complex, the alternative method described on p. 724 is to be preferred; this method showed the α-cellulose content to be 82—83%.

The substances extracted from the cellulose-complex by means of boiling dilute alkali solution showed no reducing properties. This method of resolving the cellulose-complex was not considered very promising, because most monosaccharides and polysaccharides are unstable in the presence of dilute alkalis (compare Nef, *Annalen*, 1914, **403**, 204; Nef, Hedenburg, and Glattfeld, *J. Amer. Chem. Soc.*, 1917, **39**, 1618; Glattfeld and Hawke, *ibid.*, 1918, **40**, 973). Subsequent hydrolysis of the alkaline extract with 1% sulphuric acid at 130—140° gave a solution possessing strong reducing properties.

A more promising method of attack was that of hydrolysis with dilute sulphuric acid, and by this means it has been possible to identify the more important constituents of the cellulose-complex. An attempt to break down the complex by means of 5% sulphuric acid at 100° showed that it is very resistant to acid hydrolysis, for the syrup obtained from the neutralised hydrolysis liquors, when dried under diminished pressure, amounted to only 3% of the material taken.

By treatment with 1% sulphuric acid at 130—140° the breakdown was more complete. Thus, in one experiment, 100 g. of air-dried fibre yielded a syrup soluble in 90% alcohol, weighing 12·8 g. after drying. This syrup possessed a total reducing-sugar content of 61·7%, calculated as glucose. It was possible to identify glucose, galactose, xylose, and fucose among the products of hydrolysis. On analysis, the following results were obtained: free pentose (as xylose), 10·4; methylpentose (as fucose), 9·4; galactose, 14·8, 16·3; glucose, 29·7%. With more concentrated sulphuric acid (3 and 5%), the yield of syrup was greater, mainly owing to the more extensive production of glucose. The non-reducing constituents of the syrup obtained in the acid hydrolysis have not been identified. In part, they may arise by the further action of the acid on the sugars produced by hydrolysis, for Davis and Daish (*J. Agric. Sci.*, 1913, **5**, 437) have shown that the hydrolysis of maltose by means of 2—4% hydrochloric acid at 100° is accompanied by the decomposition of a considerable amount of the resulting hexoses.

The glucose produced by hydrolysis at 130—140° in all probability is not entirely due to the breakdown of the cellulose. This is shown by the comparison, given on p. 727, of the results obtained before and after the cellulose-complex has been extracted with boiling alkali.

The resistance of the cellulose-complex to hydrolysis with 5% sulphuric acid at 100° suggests that the sugar groups are attached to the cellulose by a linkage of a glucosidic nature (compare Mehta, *Biochem. J.*, 1925, **19**, 958. Lignocellulose also is very resistant to hydrolysing agents and from this it is assumed to be a glucoside). The " -uronic anhydride " content of the cellulose complex (compare Ling, Nanji, and Paton, *loc. cit.*) is about 1·5%, amounting therefore to some 10% of the non-cellulosic constituents. Only traces of " -uronic anhydride " were found among the products of hydrolysis, but these groups are stated to be unstable to dilute acids at high temperatures (compare O'Dwyer, *Biochem. J.*, 1926, **20**, 657) and are completely decomposed by 12% hydrochloric acid at 100°.

Finally, the hydrolysis of the cellulose-complex by water has been investigated. At 100°, the action of the water was negligible, but at 140—150° a loss in weight of some 6% was produced, the hydrolysis being completed in less than 3 hours. The water-soluble products of hydrolysis consisted of (*a*) a hemicellulose, insoluble in 70% alcohol, amounting to some 4% of the weight of the fibre, (*b*) a resinous substance soluble in 70% alcohol, amounting to about 1% of the weight of the fibre.

The hemicellulose was finally obtained as a white, hygroscopic powder, containing some 21% of " -uronic anhydride " groups and possessing a neutral reaction. Careful hydrolysis with dilute sulphuric acid showed the presence of galactose and rhamnose groups, but no other sugars could be detected. Proximate analysis yielded the following results; galactose, 60; methylpentose (as rhamnose), 10·8—14·2; free pentose, 0—4; -uronic anhydride, 20·6; ash (mainly CaO), 4·8%.

The hemicellulose was not identical with the pectin extracted from flax-straw by Ehrlich (*loc. cit.*) by the action of water under pressure, as this substance contained more than 60% of " -uronic anhydride."

The soluble resinous substance was not obtained in a pure state, but on hydrolysis with dilute sulphuric acid it yielded about 25% of pentoses, and the residue was a resin of acid nature which has not been further investigated. The pentoses have been identified as fucose and xylose, present in equivalent amounts. The resinous substance contained neither galactose nor " -uronic anhydride " groups.

The fibre after extraction with water at 140—150° was still quite strong, and the cellulose was not apparently attacked. Extraction with water at higher temperatures was carried out, but even at 170° the subsequent loss in weight amounted to only about 3—4%, although the fibre was weakened considerably. The aqueous extract has been examined, but no appreciable amount of non-cellulosic substances has been isolated. This is somewhat surprising in view of the fact that the fibre after extraction with water at 140—150° still contains some 10% of substances soluble in dilute sodium hydroxide solution at 100°, and also that the "-uronic anhydride" content of the fibre is still about 0·7%.

It would seem that the non-cellulosic portion of the flax fibre is made up, in part, of a hemicellulose bound to the cellulose either by a glucosidic linkage or by means of the carboxyl of the "-uronic anhydride" group. The residual non-cellulose material is evidently very firmly fixed to the cellulose, but its nature has not yet been characterised.

EXPERIMENTAL.

Preparation of the Clean Fibre.—The fibre was obtained from unretted straw (Somerset 1923 crop—good quality) by breaking, scutching, and combing. The last operation removed most of the residual woody tissues. The root and bough ends of the fibre were discarded and the residue was subjected to the action of a dilute (0·5%) soap solution at 80° for 60 minutes, washed in water, and again leached with soap solution at 80° for 90—120 minutes. Washing was carried out by means of successive steeps in hot water until the wash-water was colourless. The loss in weight produced by this soap treatment amounted to some 25—30%, varying according to the thoroughness of the preliminary mechanical treatment. The fibre, after being dried at room temperature, was extracted with ethyl alcohol–benzene for 6 hours, and then with a 0·5% solution of ammonium oxalate at 95° for 24 hours in order to remove the pectin (Norris and Schryver, *Biochem. J.*, 1925, **19**, 676). It was then washed, and kept for 24 hours, with occasional agitation, in a cold 4% solution of sodium hydroxide, in order to remove free hemicelluloses (Norris and Schryver, *Biochem. J.*, 1925, **19**, 676). Finally, it was thoroughly washed and allowed to dry at room temperature. A sample of the fibre was given a further extraction with ammonium oxalate at 95° for 24 hours, but the liquor was free from pectin.

Isolation of a Hemicellulose from the 4% Aqueous Sodium Hydroxide Extract.—The alkaline mother-liquor was filtered from the purified fibre-strands, and again through glass wool. The pale yellow liquor possessed no reducing properties; a small portion, acidified with acetic acid, was treated with calcium chloride, but no gel was precipitated. It was therefore assumed that pectic acid was not present in the solution.

The main portion was rendered distinctly acid with acetic acid and 1·5 volumes of 90% alcohol were added (compare O'Dwyer, *Biochem. J.*, 1923, **17**, 500), whereupon a pale brown gel was slowly precipitated. This was filtered off and redissolved in the minimum amount of hot water; the opalescent solution was allowed to cool, and the hemicellulose precipitated by addition of alcohol as before. These operations were repeated and the precipitate was kneaded successively with 70%, 90%, and 98% alcohol and finally with ether. It was then exposed to the air for a short time and finally dried in a vacuum over phosphorus pentoxide. The very pale brown powder thus obtained darkened slowly on exposure to the air, was soluble in hot water, and possessed no reducing properties. It gave the pentose reaction with phloroglucinol and hydrochloric acid, and Tollens's naphtharesorcinol reagent (*Ber.*, 1908, **41**, 1788) also gave a positive reaction, indicating the presence of " -uronic anhydride " residues.

An attempt to purify the hemicellulose by the method of Baker and Pope (J., 1900, **77**, 696) proved unsuccessful, as the blue copper complex dissolved when washed with the dilute alkali.

The yield of the purified hemicellulose was approximately 1% of the weight of the fibre [Found in different preparations : C, 41·8, 41·5; H, 6·5, 5·5 (on ash-free basis); ash, 3·4, 3·6; " -uronic anhydride," 22·8, 22·7, 22·85%].

Cellulose Content of the Fibre-Complex.—(*a*) Estimations by Cross and Bevan's method gave : Total cellulose, 88·5; α-cellulose, 76·5%. (*b*) The purified fibre lost 15—16% in weight by the action of 2% sodium hydroxide solution at 100° for 24 hours. After washing, it was immersed in a cold dilute solution of sodium hypochlorite (containing 0·7 g. of available Cl per litre) for 24 hours, and the residual non-cellulosic substances were removed by the action of 1% sodium carbonate solution at 100° for 2 hours. The loss in weight amounted to less than 2%. From these figures, it appears that the α-cellulose content of the dry purified fibre-strands amounted to 82—83%.

The " -uronic anhydride " content of the cellulose-complex amounted to about 1·8—2·0%; after extraction with 2% sodium hydroxide solution at 100° for 24 hours, the " -uronic anhydride " content, estimated by the method of Ling, Nanji, and Paton, had fallen to about 0·4%.

Extraction of the Cellulose-Complex with Dilute Alkali Solution at 100°.—A sample of the purified fibre-strands lost 15% in weight (allowing for moisture content) after extraction with 2% barium hydroxide solution at 100° for 5 hours.

The air-dried fibre (80 g.) was extracted at 100° for 5 hours with

700 c.c. of the barium hydroxide solution, and the mixture then filtered. The orange-coloured liquor did not reduce Fehling's solution; after neutralisation with sulphuric acid and filtration, the liquor was decolorised with norit and hydrolysed with 1% sulphuric acid at 130—140° for 3 hours. The liquor was then neutralised with barium carbonate, and the filtrate concentrated under diminished pressure to a brown syrup (10·6 g. after drying under diminished pressure over sulphuric acid), which possessed reducing properties. The total reducing-sugars (calculated as glucose) amounted to only 24·5% of the weight of the syrup. The syrup gave positive reactions for pentoses, but only small amounts of these were present. Galactose was isolated from the syrup by means of its α-methylphenylhydrazone (needles, m. p. 190°); a mixed melting point with an authentic specimen showed no depression. The galactose content of the syrup was estimated by oxidation to mucic acid by means of nitric acid (*d* 1·15) [A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren" (Borntraeger, Berlin), 1920, p. 123]: 2·13 g. of dry syrup gave 0·148 g. of mucic acid, m. p. 213° (*op. cit.*, p. 106); galactose, 9·8%. The syrup was not further examined.

Hydrolysis of the Cellulose-Complex with Dilute Sulphuric Acid.—(1) *At* 100° *with* 5% *sulphuric acid.* The air-dried fibre (50 g.) was immersed in 300 c.c. of 5% sulphuric acid, and the mixture was warmed for 2 hours on a boiling water-bath, maintained at 100° under reflux for 5 hours, cooled, and filtered. The residual mass was well washed with water, and the washings and filtrate were warmed on the water-bath and neutralised with powdered barium carbonate. The mixture was filtered, and the mother-liquor concentrated under diminished pressure to a brown syrup. This, together with the dry precipitate, was extracted three times with boiling 90% alcohol, and the extract filtered rapidly; the filtrate was warmed with norit and concentrated to a syrup, which was finally dried in a vacuum over sulphuric acid. The yield was 1·5 g. of a brown syrup which gave the pentose reaction with phloroglucinol and hydrochloric acid.

The pentose content of the purified fibre-strands, estimated by the Kruger–Tollens–Krober method (van der Haar, *op. cit.*, pp. 63—83), amounted to 3·4%; only 180 c.c. of distillate were collected in these pentose estimations, as recommended by Klingstedt (*Z. anal. Chem.*, 1925, **66**, 129).

(2) *At* 130—140° *with* 5% *sulphuric acid.* (a) The air-dried fibre (25 g.) was immersed in 300 c.c. of 5% sulphuric acid and heated in an autoclave for 2½ hours at a pressure of 30—40 lb.

per sq. inch. The mixture was then cooled, filtered, and subjected to the treatment outlined in the previous experiment. The yield of syrup soluble in 90% alcohol was 4·8 g. after drying to constant weight in a vacuum over sulphuric acid [Found : free pentose (as xylose), 6·1; methylpentose (as fucose), 6·2; galactose, 11·5; total reducing-sugars (as glucose), 47%].

Examination of the insoluble barium salts. These were extracted three times with boiling water and the filtrate was nearly neutralised with dilute sulphuric acid, filtered, and concentrated under diminished pressure, yielding a small amount of a syrup which gave a positive reaction for " -uronic anhydride " with Tollens's naphtharesorcinol reagent. Attempts were made to isolate the " -uronic acid " as the cinchonine salt, but without success.

(b) The air-dried fibre (100 g.) was hydrolysed with 600 c.c. of 5% sulphuric acid as before, and after the usual treatment the syrup soluble in 90% alcohol weighed 27 g. It was dark brown, and this colour was not completely removed by boiling the aqueous solution of the syrup with norit [Found : free pentose (as xylose), 10·4; methylpentose (as fucose), 6·8; galactose, 7·0%].

(3) *At* 130—140° *with* 1% *sulphuric acid.* The air-dried fibre (100 g.) was hydrolysed with 600 c.c. of 1% sulphuric acid as before, at a pressure of 30—40 lb. per sq. inch, for 3 hours. The yield of yellowish-brown syrup was 12·8 g. [Found: free pentose (as xylose), 10·4; methylpentose (as fucose), 9·7; galactose, 14·8, 16·3; glucose (by fermentation), 29·7; total reducing-sugars (as glucose), 61·7%]. The glucose was estimated by fermentation with yeast for 3 hours at 35° in a Lohnstein apparatus.

Identification of Monosaccharide Groups.—(a) *The hexose groups.* Glucose was identified as the *p*-nitrophenylosazone, m. p. 250°; galactose as the α-methylphenylhydrazone, m. p. 190°, and as the *o*-tolylhydrazone, m. p. 175°. The absence of fructose in the syrup was ascertained by the fact that Pinoff's reagent (van der Haar, *op. cit.*, p. 91) gave no colour when warmed with the syrup.

(b) *The pentose groups.* Many of the typical pentose reactions are obscured by the presence of hexoses in large amount; the pentoses were accordingly separated from the dry syrup (10 g.) by two extractions with boiling absolute alcohol (20 c.c.), the extract being filtered after cooling. Galactose and glucose are sparingly soluble in this solvent, whereas the pentoses are moderately easily soluble. The extract was concentrated to small bulk, and the product gave positive pentose reactions with Bial's reagent and Neumann's reagent; a spectroscopic examination of the latter colour indicated a strong band in the red, the absorption being weaker in the yellow part of the spectrum. This indicates the presence of xylose, and confirmation was obtained by means of Bertrand's reaction (*idem, ibid.*, p. 58), whereby the characteristic boat-shaped crystals of the cadmium bromide–cadmium xylonate ($CdBr\cdot C_5H_9O_6,H_2O$) were obtained after one crystallisation. Fucose was identified in the extract, by means of the α-methylphenylhydrazone (microcrystalline, rectangular plates, m. p. 181°) and the *as*-diphenylhydrazone (microscopic needles, m. p. 193—194°). The melting points given in the literature (*idem, ibid.*, p. 207) are 180° and 197—198°, respectively. As the m. p. of galactose α-methylphenylhydrazone has been recorded as 180° (compare von Ekenstein and de Bruyn, *Rec. trav. chim.*, 1896, **15**, 97, 225), the melting point of a mixture of galactose α-methylphenylhydrazone and the above α-methylphenylhydrazone was determined; the mixture melted indefinitely at 170—176°. Further confirmation was obtained by analysis of the α-methylphenylhydrazone (Found: C, 58·7; H, 7·1. Calc. for $C_{13}H_{20}O_4N_2$: C, 58·2; H, 7·4%).

The Presence of Glucose among the Products of Hydrolysis of the Non-cellulose Portion of the Complex.—The results summarised in Table I indicate that the glucose produced by the hydrolysis of the cellulose complex is derived in part from the non-cellulose constituents. In experiments (*a*), (*d*), and (*e*), the hydrolysis product was examined for galactose, but no trace of this sugar could be detected.

TABLE I.

Hydrolysis Experiments at 130—140°.

Material.	Hydrolysing agent.	% Glucose produced on dry wt. of material.	% Total reducing sugars (as glucose) on wt. of syrup.
(*a*) Purified fibre-strands after extraction with dilute sodium hydroxide solution at 100°	1% H_2SO_4	2·76	51·6
(*b*) Purified fibre-strands	1% H_2SO_4	4·30	61·7
(*c*) Purified fibre-strands	3% H_2SO_4	9·33	58·3
(*d*) Bleached linen	1% H_2SO_4	2·83	71·0
(*e*) Bleached linen	3% H_2SO_4	3·83	

Action of Water upon the Cellulose-Complex. Preliminary Experiments.—The fibre used in this investigation contained some 3·1% of total pentoses, 1·9% of methylpentose, 2·1% of "-uronic anhydride," and some 13·5% of substances soluble in 2% sodium hydroxide solution at 100°. The results in Table II were obtained on extraction with water at various temperatures.

The residual fibre after extraction at 140—150° for 3 hours contained 1·65% of total pentoses, 0·5% of methylpentoses, 0·7% of

TABLE II.

Temp. of extraction.	Time of extraction (hrs.).	% Loss in weight.
100°	6	0·3
115—120	6	1·0
140—150	3	6·5
140—150	6	5·8
140—150	12	6·3

"-uronic anhydride," and some 10·6% of substances soluble in 2% sodium hydroxide solution at 100°.

Action of Water at 140—150°. *Isolation of Hydrolysis Product Insoluble in* 70% *Alcohol.*—The fibre (about 200 g.) was extracted with water at 100° for 3 hours, washed with water, and then heated in an autoclave with 1200 c.c. of water for 3 hours at a pressure of 50—60 lb. per sq. inch. The aqueous liquors were collected, and concentrated to about 200 c.c. After treatment with norit and the addition of about 600 c.c. of 90% alcohol, a pale brown, flocculent substance was precipitated; this was separated by filtration, the filtrate being retained. The pale brown precipitate was redissolved in warm water, and the yellow solution treated with norit. This removed some of the colour, and after addition of alcohol the precipitate was nearly colourless. The process was repeated, the precipitate next leached successively with 90% alcohol, absolute alcohol, and ether, and finally dried in a vacuum over sulphuric acid. The colourless powder thus obtained was hygroscopic and easily soluble in water, giving a pale yellow solution. The yield of the pure substance amounted to some 3·5% on the weight of the fibre, but the crude substance was obtained in 5% yield. The aqueous solution gave no precipitate with dilute acids, alkalis, or salts such as calcium chloride or lead acetate, either in neutral or in dilute acetic acid solution. It did not reduce Fehling's solution on boiling. The Tollens naphtharesorcinol test gave evidence of the presence of "-uronic anhydride" groups and also a violet colour indicating the presence of rhamnose, which was confirmed by the Rosenthaler test (*Z. anal. Chem.*, 1909, 48, 167; van der Haar, *op. cit.*, p. 48). Ketose groups were not present, as determined by Pinoff's test. The substance contained some 4·8% of ash which consisted mainly of calcium oxide. This ash was not easily removed, although the aqueous solution of the hemicellulose gave a crystalline precipitate with ammonium oxalate.

Analysis.—(1) The hemicellulose was dried in a vacuum over phosphorus pentoxide for each determination [Found: C, 42·5; H, 6·1 (on ash-free basis); ash, 4·7%].

(2) A sample was dissolved in water and a small amount of dilute acetic acid added; after two precipitations with alcohol, it

was dried as before [Found : C, 42·7, 42·8; H, 6·2, 5·9 (on ash-free basis); ash, 1·8, 1·8%].

" -Uronic anhydride " estimations. Found : " -Uronic anhydride," 20·8, 20·85, 20·3%.

Galactose estimations. The yield of mucic acid corresponded to 78% of galactose and galacturonic anhydride. Assuming that the " -uronic anhydride " group gave a 60% yield of mucic acid * the amount of galactose present in the hemicellulose would be about 60%.

Pentose estimations. In these estimations allowance was made for the " -uronic anhydride " group, which was assumed to give a 30% yield of phloroglucoside (van der Haar, *op. cit.*, p. 75) [Found : free pentose, 4·3, trace; methylpentose (as rhamnose), 10·5, 14·2%].

Hydrolysis of Hemicellulose.—Preliminary experiments were carried out on the action of dilute sulphuric acid at 100° upon the hemicellulose, the total reducing-sugars (calculated as glucose) being estimated by Pavy's method. The maximum yield of total reducing-sugars after 6 hours amounted to less than 60% and the liquor was brown, indicating decomposition of the products of hydrolysis. Hydrolysis for 3 hours with 1% sulphuric acid at 130—140° gave a yield of 83% of reducing sugars (as glucose).

Examination of the Products of Hydrolysis.—A solution of the hemicellulose (8·5 g.) in 250 c.c. of 2% sulphuric acid was heated for 7 hours on the boiling water-bath and at 130—140° for 1½ hours, and the liquor was neutralised with powdered barium carbonate and filtered. The filtrate, pale yellow after treatment with norit, gave a positive reaction for " -uronic anhydride " with Tollens's naphtharesorcinol reagent and reduced Fehling's solution in the cold. It was concentrated to a syrup under diminished pressure, and this syrup extracted twice with boiling absolute alcohol.

The alcoholic extract slowly deposited long, colourless crystals, m. p. 159°; a mixture of this substance with pure *d*-galactose melted at 159°. A small portion was converted into the α-methylphenylhydrazone (m. p. 190°).

The galactose was filtered from the alcoholic liquor, and the latter concentrated to a syrup under diminished pressure. This syrup gave positive tests for rhamnose with Tollens's naphtharesorcinol reagent and Rosenthaler's reagent. Neumann's orcinol test gave a pale yellow coloration, indicating the absence of free pentoses.

Rhamnose was identified as the *p*-nitrophenylosazone, a dark red precipitate which, after being dissolved in pyridine and reprecipitated with ether, melted at 234—235°. The phenylosazone also was prepared (m. p. 179—180°). Van der Haar (*op. cit.*, p. 227) gives m. p. 236° and 162°, respectively.

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* Ehrlich and Schubert (*Biochem. Z.*, 1926, **169**, 57) state that oxidation of *d*-galacturonic acid with bromine water gave a 60% yield of mucic acid.

No other hexoses or pentoses could be detected among the products of hydrolysis. The nature of the "-uronic anhydride" group was not ascertained with precision, although it is evident, from the yield of mucic acid produced by the oxidation of the hemicellulose, that "galacturonic anhydride" is a component of this substance. The residue from the absolute-alcoholic extraction was dark brown and semi-solid. It was dissolved in water, and to the filtered solution 90% alcohol (4 vols.) was added, whereby a flocculent, pale yellow substance was precipitated. This was washed with absolute alcohol and ether and dried in a vacuum over sulphuric acid. The yield of the pale yellow powder was 0·5 g., the small yield being explained by the fact that *d*-galacturonic acid is unstable under the conditions of hydrolysis (see O'Dwyer, *Biochem. J.*, 1926, **20**, 657) [Found: Ba, 25·7. Calc. for $(C_6H_9O_7)_2Ba$: Ba, 26·2%]. An attempt to isolate crystalline *d*-galacturonic acid by Ehrlich's method (Ehrlich and Schubert, *loc. cit.*) was unsuccessful, a small amount of a syrup being produced, from which no crystalline cinchonine salt could be isolated. The syrup possessed strong reducing properties, even at the ordinary temperature.

Many modifications of the conditions of hydrolysis were made, but in no case was the yield of barium *d*-galacturonate greater than that produced above, and from the accumulated yield it was not possible to prepare crystalline *d*-galacturonic acid or its cinchonine salt. It is possible that a small amount of *d*-glycuronic acid may be present, which may inhibit crystallisation.

Action of Water at 140—150°. *Isolation of a Hydrolysis Product Soluble in* 70% *Alcohol.*—The brown 70% alcoholic mother-liquor, after removal of the insoluble hemicellulose described above, was concentrated to a syrup under diminished pressure, and the syrup dried to constant weight in a vacuum over sulphuric acid. The yield was approximately 1% of the weight of the fibre.

The syrup was dark brown, and gave a negative reaction for "-uronic anhydride." The presence of pentoses was indicated by Neumann's reagent, an olive-green coloration being obtained. Oxidation of a portion of the syrup with nitric acid (*d* 1·15) yielded no mucic acid, and therefore galactose was assumed to be absent [Found: free pentose (as xylose), 12·0; methylpentose (as fucose), 11·9%].

Hydrolysis of the syrup. The syrup was mixed with 100 c.c. of 1% sulphuric acid; it was not completely soluble, a small amount of dark brown substance remaining undissolved at the end of the hydrolysis. The mixture was heated on the water-bath for 4 hours, norit added, and the mixture filtered. The filtrate was concentrated to a syrup under diminished pressure, and extracted (*a*) with boiling 98% alcohol, (*b*) with 80% alcohol. Fucose and xylose were identified in (*a*) by the methods previously described. No hexoses or pentoses were present in (*b*); the liquor on concentration gave a resinous substance, acid to litmus and insoluble in organic solvents other than aqueous alcohol, which was not further examined.

Action of Water at Higher Temperatures.—The fibre which had already been extracted with water at 130—140° was extracted with water at temperatures up to 170°. The aqueous extract, on concentration to small bulk, yielded only a small amount of a substance insoluble in 80% alcohol. By evaporation of the aqueous extract to dryness under diminished pressure, a small amount of a dark syrup was produced; this possessed slight reducing properties. The fibre lost some 3—4% in weight on extraction with water at 160—175° for 2 hours and was appreciably weakened. At temperatures above 175°, the fibre was disintegrated and the residue was very dark in colour.

It is proposed to examine the products obtained by the action of dilute alkali solution at 100° upon fibre which has been extracted with water at 135—140°. The fibre loses some 10% in weight by this treatment.

In conclusion, the author expresses his thanks to the Linen Industry Research Association for permission to publish the results of this investigation, and also to Dr. W. H. Gibson and Mr. C. R. Nodder for their kind interest and helpful suggestions.

THE LINEN INDUSTRY RESEARCH ASSOCIATION,
LAMBEG, CO. ANTRIM.
[*Received, January 21st*, 1927.]

CVII.—*Constituents of* Myoporum Lætum, *Forst.* (The "Ngaio"). *Part II. Hydrogenation of Ngaione and Ngaiol and Dehydration of Ngaiol.*

By FREDERICK HENRY MCDOWALL.

THE presence of two double bonds in ngaione (J., 1925, 2200) has now been confirmed by the process of hydrogenation with Paal's colloidal palladium. Both ngaione and ngaiol, the secondary alcohol obtained from it by reduction, take up four atoms of hydrogen to form saturated *tetrahydro*-derivatives, $C_{15}H_{26}O_3$ and $C_{15}H_{28}O_3$. Tetrahydrongaione was characterised by the crystalline *picrolonate* of *tetrahydrongaiylamine*, obtained from the ketone by reduction of its liquid oxime.

Attempts to obtain a dioxide from ngaione- and tetrahydrongaione-hydrazones by the methods of Woulff and Kishner have been unsuccessful.

The action of dehydrating agents on ngaiol has been exhaustively investigated. Concentrated formic acid at the boiling point gave a 50% yield of *ngaiol formate* [compare citronellol, which by this treatment gives citronellol formate almost quantitatively (Schimmel & Co., Report, 1901, 47), and caryophyllene, which with formic acid gives the formate of caryophyllene alcohol (Robertson, Kerr, and Henderson, J., 1925, **127**, 1944)]. On treatment with potassium hydrogen sulphate, ngaiol loses a molecule of water, to form *dehydrongaiene dioxide*,* $C_{15}H_{22}O_2$, but the yield is not large. *Ngaiylamine* was prepared from ngaioneoxime by reduction with sodium and alcohol, and converted into the phosphate. This, on dry distillation in a vacuum according to the method of Harries (*Annalen*, 1903, **328**, 91), yielded no product. Dilute aqueous (2*N*), 50% aqueous, and 10% alcoholic sulphuric acid caused racemisation and a slow change to a dehydrated compound, while complete resinification took place with 50% alcoholic sulphuric acid at 60—70° and with 80% aqueous sulphuric acid at 0°. This is in marked contrast to the behaviour of calameone, $C_{15}H_{26}O_2$, which easily loses two molecules of water when boiled for ½ hour with 10% aqueous sulphuric acid (Thoms and Beckström, *Ber.*, 1902, **35**, 3187). The best method of obtaining dehydrongaiene dioxide is by the action of alcoholic potash on the unstable *chloride*, formed by the action of thionyl chloride and pyridine on ngaiol.

Dehydrongaiene dioxide has a molecular refractivity corresponding to the presence of three double bonds, and with colloidal palladium takes up three molecules of hydrogen, yielding *tetrahydrongaiene dioxide*, $C_{15}H_{28}O_2$. The remarkable stability of two of the oxygen atoms in ngaiol to the action of dehydrating agents lends strong support to the conclusion that they are oxidic in character. They are not immune, however, from attack by oxidising agents, and it is hoped in a later publication to describe their behaviour on oxidation.

If Skita's colloidal palladium or platinum be used instead of Paal's palladium for the hydrogenation of ngaiol, the product contains a considerable proportion of a *glycol*, $C_{15}H_{30}O(OH)_2$, evidently formed through fission of one of the oxide rings by the hydrogenating agent. Since no trace of such a compound has been obtained in the course of numerous experiments with Paal's colloid, it seems probable that the formation of the glycol is due to the slight acidity of Skita's reagent.

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* The nomenclature is based on the hypothetical sesquiterpene, ngaiene, $C_{15}H_{24}$, corresponding to ngaione.

EXPERIMENTAL.

(a) *Hydrogenation.*—The hydrogen burette used was modelled on that of Francke (*Chem. Ztg.*, 1913, **37**, 958), the leading-tubes through rubber bungs being replaced by direct seals to a calibrated, thick-walled glass tube of about 5 cm. bore. The shaking-bottle was an ordinary 750 c.c. reagent bottle fitted with a hollow, ground-glass stopper joined to a tap and leading-tube, and held in by a clamp which gripped the top shoulder of the stopper.

The following modifications considerably decreased the tendency of the catalyst to become poisoned and lose its activity. During the preliminary evacuation, and also during the hydrogenation, alcohol vapour is drawn up and condenses in the rubber tubing; on the introduction of the hydrogen stream, this flows back into the hydrogenation bottle, carrying with it minute particles of rubber. A small inverted Kjeldahl trap was inserted on the leading-tube above the tap to prevent the reflux of any liquid that had been in contact with rubber, and a plug of cotton wool was inserted above the bulb to remove particles of rubber from the hydrogen stream. In default of a flexible copper connexion (Skita, *Ber.*, 1912, **45**, 4594), these precautions were found to ensure fairly regular results. Small particles of rubber were apt to be carried back from the side-tube of the receiver during the distillation at low pressure previous to hydrogenation. This defect was remedied by the use of a small Kjeldahl trap and a plug of glass wool in the side-tube of the external receiving tube.

Tetrahydrongaione. A suspension of ngaione (10 g., fractionally distilled at reduced pressure, and distilled again from a metal-bath immediately before use) in 100 c.c. of 50% ethyl alcohol was treated with a solution of Paal's colloidal palladium containing 0·05 g. of metal, and shaken with hydrogen at 1½ atm. pressure. The rate of absorption decreased steadily from the beginning, and several additions of fresh colloid were required during the course of the experiment. In the best circumstances, one molecular proportion was absorbed in 2½ hours, and further shaking for 10 hours completed the reaction. It was usually necessary, however, to extract and redistil the oil and to hydrogenate it with fresh colloid at least once before complete saturation could be reached. *Tetrahydrongaione* was obtained in 80% yield as a colourless, odourless oil, b. p. 196—198°/29 mm., $d_{20^\circ}^{20^\circ}$ 0·9977, $[\alpha]_D$ − 5·41°, $n_D^{20^\circ}$ 1·4652; $[R_L]_D$ 70·42 (calc. for $C_{15}H_{26}O_3$: $[R_L]_D$ 70·38) (Found: C, 70·6; H, 10·4.

$C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%). No trace of tetrahydrongaiol was observed in the product of hydrogenation.

The p-*nitrophenylhydrazone* and *oxime* were prepared as viscous liquids. The *semicarbazone* slowly crystallised to a waxy mass, but could not be recrystallised. Tetrahydrongaione oxime was therefore converted by reduction with sodium and alcohol into *tetrahydrongaiylamine*, a colourless, limpid oil with a strong odour, b. p. 198—200°/29 mm., $d_{20^\circ}^{20^\circ}$ 0·968, $n_D^{20^\circ}$ 1·4718, $[R_L]_D$ 73·82 (calc. for $C_{15}H_{29}O_2N$: $[R_L]_D$ 73·78) (Found: C, 70·1; H, 11·6; N, 5·5. $C_{15}H_{29}O_2N$ requires C, 70·5; H, 11·5; N, 5·5%). *Tetrahydrongaiylamine picrolonate* was prepared in alcoholic solution and separated, after three crystallisations from alcohol, in bright yellow prisms, m. p. 184—185° (Found: N, 13·7. $C_{25}H_{37}O_7N_5$ requires N, 13·5%).

Dihydrongaiol. Ngaiol, purified through the acid phthalate (see Part I, *loc. cit.*), was treated as above described, the reaction being interrupted after the absorption of one molecule of hydrogen. Repeated distillation of the resulting oil yielded *dihydrongaiol*, a colourless, odourless oil, b. p. 199—202°/28 mm., $d_{20^\circ}^{20^\circ}$ 1·0009, $[\alpha]_D$ − 11·73°, $n_D^{20^\circ}$ 1·4702, $[R_L]_D$ 70·86 (calc. for $C_{15}H_{26}O_3|\overline{_1}$: $[R_L]_D$ 71·41) (Found: C, 70·9; H, 10·6; *M*, cryoscopic in benzene, 254. $C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%; *M*, 254). Acetylation yielded a *monoacetate*, a light yellow oil, b. p. 192°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·0152, $n_D^{20^\circ}$ 1·4631, $[R_L]_D$ 80·42, saponification value (by direct titration after saponification with absolute alcoholic potash), 186 ($C_{15}H_{25}O_2{\cdot}OAc|\overline{_1}$ requires $[R_L]_D$ 80·78; S.V. 189).

Tetrahydrongaiol, the product of complete saturation of ngaiol with hydrogen under the above conditions, was obtained as a colourless, almost odourless, viscous oil, b. p. 202—206°/29 mm., $d_{20^\circ}^{20^\circ}$ 0·9917, $[\alpha]_D$ + 2·96°, $n_D^{20^\circ}$ 1·4674, $[R_L]_D$ 71·76 (calc. for $C_{15}H_{28}O_3$: $[R_L]_D$ 71·88) (Found: C, 70·2; H, 11·0; *M*, cryoscopic in benzene, 264. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%; *M*, 256). The product was free from glycol (see hydrogenation with Skita's reagent, later). Reduction of tetrahydrongaione with sodium and alcohol gave tetrahydrongaiol with physical constants almost identical with those recorded. The phenylurethane was obtained as a viscous syrup which did not crystallise even after removal of all adhering oil by distillation in steam.

Tetrahydrongaiol slowly decolorised aqueous potassium permanganate, but was quite unaffected by bromine in aqueous ether. Acetylation with acetic anhydride yielded *tetrahydrongaiol acetate*, a colourless oil with a slightly sharp odour, b. p. 205°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·0096, $n_D^{20^\circ}$ 1·4615, $[R_L]_D$ 81·06, saponification value, 184 (calc. for $C_{15}H_{27}O_2{\cdot}OAc$: $[R_L]_D$ 81·25; S.V. 187).

An attempt was made to prepare a di- or tri-acetate of tetrahydrongaiol by boiling this (2 g.) with freshly-distilled acetyl chloride (10 g.). The excess of acetyl chloride was then decomposed with sodium bicarbonate, and the oil was extracted with ether, and freed from solvent in a vacuum at 100° (Saponification value of the residual brown liquid, 200. Calc. for tetrahydrongaiol monoacetate, 194). The substance distilled at 1 mm. pressure without decomposition (unchanged refractive index) as a light yellow liquid, $n_D^{20^\circ}$ 1·4682, $d_{20^\circ}^{20^\circ}$ 0·9973. A trace of chlorine was present (Found: C, 68·9; H, 10·3. $C_{15}H_{27}O_2\cdot OAc$ requires C, 68·4; H, 10·2%). These results show that only a *monoacetate* had been formed, and that no dehydration had taken place (compare calameone, which by this treatment loses two molecules of water). The physical constants of the acetate obtained by this method indicate a considerable amount of isomerisation by the strongly acid reagent.

The glycol produced by hydrogenation of ngaiol. Ngaiol (10 g.) in 250 c.c. of 60% alcohol was shaken with colloidal platinum (prepared by inoculation of 10 c.c. of a 1% solution of chloroplatinic acid with colloidal palladium according to the method of Skita) at 2 atm. pressure. Two successive treatments yielded a colourless, viscous oil, which proved on fractionation to be a mixture of mono- and di-hydroxy-compounds.

Fraction I had b. p. 185—200°/21 mm., $d_{20^\circ}^{20^\circ}$ 0·9768, $n_D^{20^\circ}$ 1·4664 (Found: C, 69·8; H, 11·4; *M*, by Rast's camphor method, 261. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0; *M*, 256. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%; *M*, 258). The acetate was prepared in the usual way with acetic anhydride, extracted with ether, and freed from ether in a vacuum at 100°. The light yellow oil thus obtained had saponification value 240. The fraction was therefore evidently a mixture of tetrahydrongaiol with an oxido-glycol.

Fraction III consisted of a fairly pure *oxido-glycol*, b. p. 217—220°/21 mm., $d_{20^\circ}^{20^\circ}$ 0·9734, $n_D^{20^\circ}$ 1·4668, $[R_L]_D$ 73·58 {calc. for $C_{15}H_{28}O(OH)_2$: $[R_L]_D$ 73·96} (Found: C, 69·7; H, 11·8; *M*, by Rast's camphor method, 250. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%; *M*, 258). The acetate, prepared as described above, was an almost colourless oil, $n_D^{20^\circ}$ 1·4550, saponification value 304 [$C_{15}H_{28}O(OAc)_2$ requires S.V. 326].

(b) *Action of Halogens and Halogen Acids.*—Ngaione and ngaiol are very sensitive to the action of halogens and halogen acids. When treated with iodine monochloride according to the Wijs method, ngaione gave the iodine value 101, and ngaiol the value 104, corresponding very closely to the theoretical values, 102 and 104, respectively, for the presence of one double bond. This failure of the Wijs method to give a correct indication of the extent of unsaturation is not unusual with constituents of essential oils, but it is of interest that in each of the above cases one double linking is so definitely indicated.

Bromine water was only slowly decolorised, whereas bromine in cooled chloroform was rapidly absorbed by ngaione, giving a black tar, with evolution of much hydrogen bromide. Bromine in hydroxylic solvents, such as ether–alcohol (1 : 1) at — 10°, and glacial acetic acid, was rapidly decolorised by ngaione, and hydrogen bromide was then copiously evolved, even before the addition of one molecule of bromine was completed. The instability of the bromine addition compounds, especially in wet solvents, would account for the slow rate of decoloration of bromine water by ngaione and ngaiol. A crystalline bromide, or even a liquid compound with the bromine content of a dibromide, was not obtained in any of the above experiments.

When gaseous hydrogen bromide or hydrogen iodide was passed into their cooled glacial acetic acid solutions, ngaione and ngaiol were rapidly and completely resinified. The action of halogen acids on tetrahydrongaione and tetrahydrongaiol will be described in a later paper.

(c) *Hydrazones of Tetrahydrongaione and Ngaione.*—It has been shown by Woulff (*Annalen*, 1912, **394**, 86) and by Kishner (*Chem. Zentr.*, 1912, I, 1713; 1913, I, 706; *et al.*) that the carbonyl group of many ketones can be replaced by a methylene group by decomposition of their hydrazones (see also Staudinger, *Ber.*, 1911, **44**, 2197).

Tetrahydrongaione easily formed a hydrazone when heated in alcoholic solution for 6 hours with an excess of 90% hydrazine. Removal of the extracting ether in a vacuum at 100° yielded a thick, colourless oil, $n_D^{20°}$ 1·4920. This decomposed to a considerable extent on distillation, with much evolution of gas, the residue being presumably a ketazine. The distillate had b. p. 210—220°/13 mm. and $n_D^{20°}$ 1·4921 (Found: N, 9·9. $C_{15}H_{26}O_2{:}N{\cdot}NH_2$ requires N, 10·4%). The low value for nitrogen was probably due to the presence of a trace of ketazine. In subsequent experiments, no attempt was made to purify the hydrazone.

When tetrahydrongaionehydrazone was heated at 120—180° with a small lump of fused caustic potash or with platinised tile (Kishner, *loc. cit.*), some evolution of nitrogen took place; no oil was obtained volatile in steam, and it was evident that the reaction had stopped at the formation of the ketazine, a very viscous oil which did not crystallise after 6 months' standing.

Tetrahydrongaionehydrazone was decomposed by alcoholic sodium ethoxide in a sealed tube at 160—165°, and at 190—200°, giving an inflammable gas, ammonia, and substances of approximate composition $C_{12}H_{22}O$ or $C_{14}H_{26}O$. Ngaionehydrazone under the same conditions formed a complex mixture of decomposition products, b. p. 120—210°/29 mm. The low-boiling portion had an odour resembling that of citral, whilst a fraction, b. p. 170—190°/29 mm., gave analytical values (C, 79·1; H, 11·2%) of no obvious meaning.

It is clear that the hydrazones are decomposed by sodium ethoxide with loss of carbon from the molecule, possibly owing to the presence of an oxide linking next to the carbonyl group. That this change is not wholly related to the oxide rings, but is an intrinsic property of the hydrazone, was shown by the fact that ngaiol remained completely unaltered, even as regards its specific rotation, when heated for 12 hours with alcoholic sodium ethoxide in a sealed tube at 160—170°.

The results suffice to show that it is not possible to obtain by this method the dioxides $C_{15}H_{24}O_2$ and $C_{15}H_{28}O_2$ from ngaione and tetrahydrongaione, respectively. The investigation of the reaction has therefore been left in abeyance until more is known of the structure of ngaione.

(d) *Action of Dehydrating Agents on Ngaiol.*—(1) *Concentrated formic acid.* Ngaiol (20 g.) was heated on the water-bath with 90% formic acid (70 g.) for 5 minutes. The acid was then neutralised with sodium carbonate, and the oil extracted with ether. Distillation gave 11 g. of a light yellow oil, b. p. 186—188°/26 mm., $d_{20°}^{20°}$ 1·0387, $n_D^{20°}$ 1·4751 (Found: C, 69·5; H, 9·0; saponification value, 162. $C_{15}H_{23}O_2{\cdot}O{\cdot}COH$ requires C, 68·5; H, 8·7%; S.V., 200. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%). The oil was thus a mixture of ngaiol and its formate, from which ngaiol was recovered with unchanged physical constants by saponification with alcoholic potash. Heating of ngaiol for ½ hour with 100% formic acid caused almost complete resinification.

(2) *Potassium hydrogen sulphate.* An intimate mixture of ngaiol (1 part) and the finely-powdered dehydrating agent (2 parts) was rapidly heated to 190° in an atmosphere of carbon dioxide. After ¼ hour, the product was cooled, and distilled in steam. Extraction of the distillate with petrol gave a 40% yield of a mixture of about equal parts of ngaiol and *dehydrongaiene dioxide*, $C_{15}H_{22}O_2$. The latter was separated by fractional distillation as an orange-coloured oil with a somewhat tarry odour, b. p. 168—174°/29 mm., $d_{20°}^{20°}$ 0·9689, $n_D^{20°}$ 1·4914, $[R_L]_D$ 70·03 (calc. for $C_{15}H_{22}O_2|\overline{\overline{3}}$: $[R_L]_D$ 68·95). The high value of the molecular refraction may be due to the presence of conjugated double bonds (Found, for two different specimens: C, 76·2, 76·4; H, 9·6, 9·3. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The substance rapidly absorbed oxygen from the air, forming a thick brown oil.

(3) *Treatment with zinc dust.* It has been shown by Semmler (*Ber.*, 1894, **27**, 2520; 1900, **33**, 776) and others (Gaudurin, *Ber.*, 1908, **41**, 4361; Ruzicka and Stoll, *Helv. Chim. Acta*, 1924, **7**, 100) that many alcohols are reducible by means of zinc dust at a high temperature. Ngaiol, however, was completely unaffected when heated with three times its weight of zinc dust at 210—220° in a sealed tube in an atmosphere of carbon dioxide, and even when heated at 250—260° for 4 hours it suffered no change other than slight decreases in the density and the optical rotation. No pressure was developed in the tube in either case.

(4) *Dry distillation of the amine phosphate.* Ngaione oxime was unaffected by sodium amalgam and acetic acid (compare Goldschmidt, *Ber.*, 1887, **20**, 486), but was easily reduced by sodium and alcohol, giving a 70% yield of *ngaiylamine*, a colourless, limpid, strongly odorous liquid which gradually turned brown in the air, b. p. 184—186°/29 mm., $d_{20^\circ}^{20^\circ}$ 0·9940, $[\alpha]_D$ $-$ 18·63°, $n_D^{20^\circ}$ 1·4822, $[R_L]_D$ 72·07 (calc. for $C_{15}H_{23}O_2{\cdot}NH_2|^{=}_{2}$: $[R_L]_D$ 72·64) (Found : C, 71·4; H, 10·2; N, 5·6. $C_{15}H_{25}O_2N$ requires C, 71·6; H, 10·0; N, 5·6%). The amine was unstable to hot hydrochloric acid, but the double compound with platinic chloride could be prepared in the cold as a bright yellow solid, decomp. 170—180° [Found : Pt, 21·4. $(C_{15}H_{23}O_2{\cdot}NH_2)_2,PtCl_4$ requires Pt, 21·4%].

Ngaiylamine hydrobromide was obtained pure, by several crystallisations from a cold concentrated solution in absolute alcohol by addition of dry ether, in long, white, rectangular prisms, m. p. 190—191° (Found : Br, 24·1. $C_{15}H_{25}O_2N,HBr$ requires Br, 24·1%). Unlike the hydrochloride, it is not hygroscopic.

Benzenesulphonngaiylamide was prepared by the Schotten–Baumann process, and the resulting oil extracted with ether. The substance crystallised in elongated, rectangular prisms, m. p. 107—108° [Found : N (micro-Kjeldahl), 3·5. $C_{21}H_{29}O_4NS$ requires N, 3·6%].

Ngaiylamine picrolonate was obtained as a yellow powder, which formed amber-coloured prisms in radiating tufts on recrystallisation from warm absolute alcohol; m. p. 162—163°, independent of the rate of heating (Found : N, 14·0. $C_{25}H_{33}O_7N_5$ requires N, 13·6%).

(5) *Treatment with sulphuric acid.* Ngaiol (6 g.) was boiled with 2*N*-sulphuric acid (40 g.) for 1 hour, and recovered, by distillation in steam, without appreciable change in physical constants other than a 50% lowering of the specific rotation. Boiling with 33% sulphuric acid for 6 hours produced a resin, and also a substance, b. p. 182—189°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·0008, $n_D^{20^\circ}$ 1·4802 (Found : C, 73·8; H, 9·5. Ngaiol, $C_{15}H_{24}O_3$, requires C, 71·4; H, 9·6%). A certain amount of

dehydration had thus taken place, but the product was impure, and the yield was small.

(6) *Dehydrongaiene dioxide prepared through ngaiyl chloride.* For the preparation of ngaiyl chloride, the Darzens process (*Compt. rend.*, 1911, **152**, 1314; Forster and Cardwell, J., 1913, **103**, 1341) was chosen as the most suitable in view of the sensitiveness of the ngaiol molecule to halogen acid (see p. 735). To a mixture of ngaiol (10·6 g.) and pure dry pyridine (3·6 g.; 1 mol.), thionyl chloride (5·4 g.; 1 mol.) was added slowly with shaking and cooling in ice. After standing for 1 hour at room temperature, the yellow product was decomposed by heating it on the water-bath for 1 hour, and the resulting oil was acidified and extracted with ether. On removal of the solvent a heavy, black, oily *chloride* was obtained which was very unstable, partly decomposing even at water-bath temperature. Distillation at 16 mm. pressure caused much decomposition with evolution of hydrogen chloride, and the distillate contained only 3% of chlorine (calc. for $C_{15}H_{23}O_2Cl$: Cl, 13·1%). The oil was therefore heated for 2 hours with *N*-alcoholic potash, and the product distilled in steam. The main portion of the resulting liquid, a yellow oil with a tarry odour, boiled at 170—175°/28 mm., $d_{20^\circ}^{20^\circ}$ 0·9751, $[\alpha]_D$ — 10·84°, $n_D^{20^\circ}$ 1·4854, $[R_L]_D$ 68·90 (calc. for $C_{15}H_{22}O_2|\overline{\underline{}}_3$: $[R_L]_D$ 68·95) (Found: C, 76·7; H, 9·5. Calc. for $C_{15}H_{22}O_2$: C, 76·9; H, 9·5%). The yield was 45% of the theoretical. (Dehydrongaiene dioxide must be prepared and kept in an atmosphere of carbon dioxide, or other indifferent gas, since it easily absorbs oxygen from the air.)

iso*Dehydrongaiene Dioxide*.—Ngaiol can also be converted into a dehydrongaiene dioxide by the use of an excess of pure dry quinoline, instead of the calculated quantity of pyridine. The formation of an *iso*-compound under these conditions may be due to the fact that the solution never becomes acid—during the decomposition on the water-bath of the complex thionyl compound described above, the resulting ngaiyl chloride is partly decomposed with evolution of hydrogen chloride.

Quinoline (20 g.; 5 mols.) was mixed with ngaiol (9·3 g.; 1 mol.) at — 15° in a flask through which a stream of dry carbon dioxide was passing, and thionyl chloride (3·1 g.; 1 mol.) was slowly added. After 1 hour, the yellow product was decomposed by heating it on the water-bath for 1 hour, and the chloride present was then further decomposed by the excess of quinoline by heating the mixture at 150—160° for 1 hour. The product was poured into dilute acetic acid and distilled in steam in a current of carbon dioxide. From the resulting oil, which still contained a small quantity of chlorine, a fraction (1 g.) was isolated, free from chlorine, b. p. 168—174°/

29 mm., $n_D^{20°}$ 1·4801, $d_{20°}^{20°}$ 0·9654, $[R_L]_D$ 68·95 (calc. for $C_{15}H_{22}O_2|\overset{=}{_3}$: $[R_L]_D$ 68·95) (Found: C, 76·8; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The physical constants indicate that the substance is an isomeride of the dehydrongaiene dioxide obtained by the use of pyridine, probably differing from it in the position of the double bond. The higher-boiling fraction consisted for the most part of unchanged ngaiol.

Tetrahydrongaiene Dioxide.—Dehydrongaiene dioxide (5·9 g.) (obtained by the pyridine method), in presence of Paal's colloidal palladium (7 c.c. of 1% solution) and 50% ethyl alcohol (100 c.c.), absorbed hydrogen only slowly, and several treatments were necessary before saturation was reached. Eventually a colourless oil was obtained, with a slight pineapple odour, b. p. 170—180°/29 mm., $d_{20°}^{20°}$ 0·9379, $n_D^{20°}$ 1·4631, $[R_L]_D$ 70·63 (calc. for $C_{15}H_{28}O_2$: $[R_L]_D$ 70·35) (Found: C, 74·9; H, 11·7. $C_{15}H_{28}O_2$ requires C, 74·9; H, 11·7%).

The author desires to thank Professor Inglis, of Otago University, New Zealand, for kindly arranging the supply of further quantities of ngaio oil. He is also indebted to the Department of Scientific and Industrial Research for a maintenance grant, and to the Chemical Society and the New Zealand Institute for grants towards the expenses of the research.

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CVIII.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XIII.*

By HUGH GRAHAM, ALEXANDER KILLEN MACBETH, and WILFRED BEAUMONT ORR.

IN the previous communication (J., 1926, 1248), it was shown that the dihalogen derivatives of a series of barbituric acids are reduced by hydrazine hydrate to the corresponding monohalogen compounds, and spectroscopic evidence was submitted which indicated that barbituric acid and its monohalogen derivatives exist in the enolic modification, whereas the dihalogen derivatives possess a definitely ketonic structure. Further support for this view has now been found in the absorption spectra of 1-phenylbarbituric acid and 1 : 3-diphenylbarbituric acid and their derivatives, the graphs for which are shown in Figs. 1—4. The parent acids and the monohalogen derivatives give absorption spectra showing well-defined bands characteristic of the enolic modification; the dihalogen compounds, on the other hand, show general absorption only.

Comparison of the various graphs shows that the spectra of the phenylbarbituric acids are of a much simpler character than the absorption spectrum of barbituric acid itself, the complex bands in the latter being replaced by a principal band extending over 1/λ 3700—4200. That this band is characteristic of the enolic modification is evident from the fact that it occurs in the presence of alkali,

FIG. 1. FIG. 2.

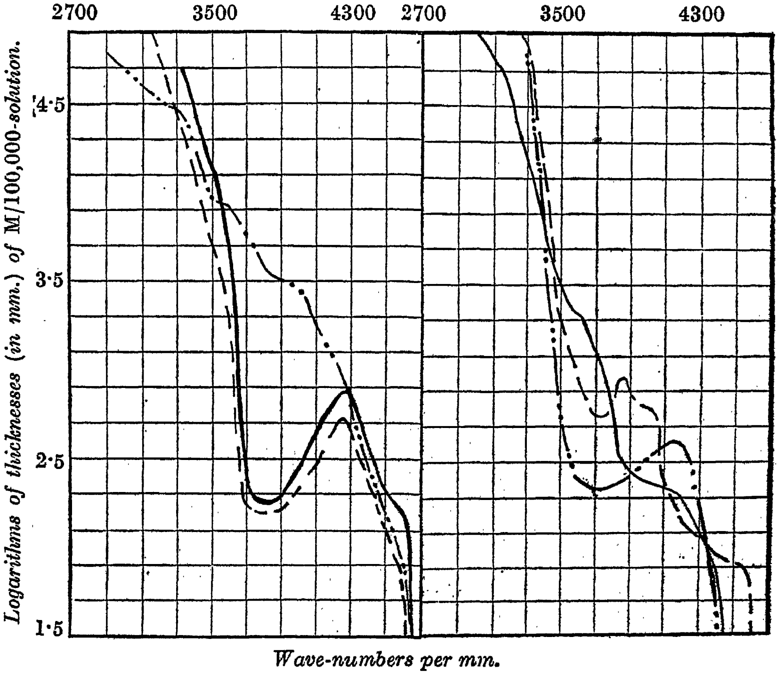


FIG. 1.

———— 1-*Phenylbarbituric acid* (*in water*).
— — — — " + NaOH.
—··—··— " + HCl.

FIG. 2.

———— 5 : 5-*Dibromo-1-phenylbarbituric acid* (*in alcohol*).
— — — — " + NaOEt.
—··—··— 5-*Bromo-1-phenylbarbituric acid* (*in water*).

and virtually disappears in the presence of hydrochloric acid; and since the band is only slightly more persistent in an alkaline solution than in an aqueous solution of the parent acids or their monohalogen derivatives, the latter also must exist in the enolic form.

The spectra of the dihalogen compounds (Figs. 2 and 4) undergo a marked change on the addition of alkali, the band characteristic of the enolic modification developing to some extent. The decomposition of the dihalogen compound to the corresponding monohalogen derivative in alkaline solution is thus indicated, and additional proof of such change is given below.

For the purpose of comparison, the work was extended to the examination of absorption spectra of typical thiobarbituric acids,

FIG. 3. FIG. 4.

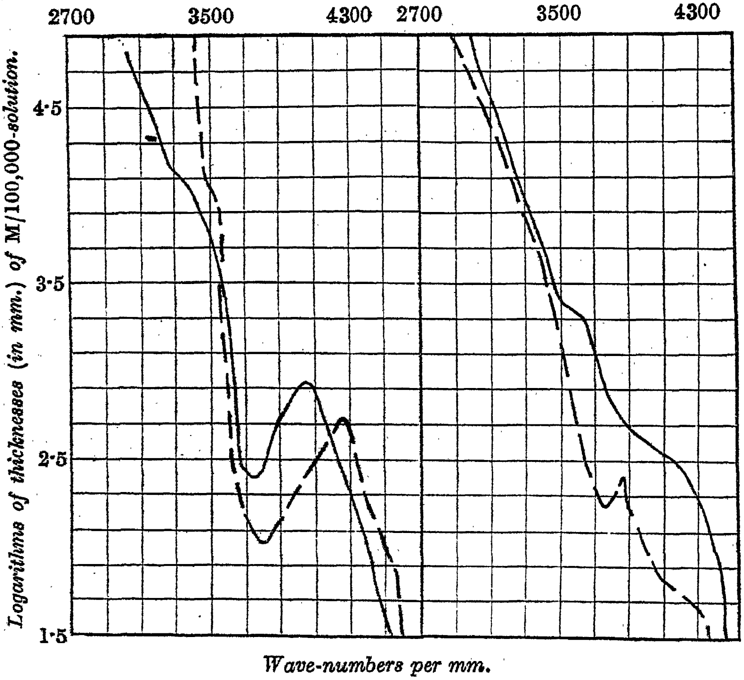


FIG. 3.

——————— 1 : 3-*Diphenylbarbituric acid* (*in alcohol*).
— — — — ″ + NaOEt.

FIG. 4.

——————— 5 : 5-*Dibromo*-1 : 3-*diphenylbarbituric acid* (*in alcohol*).
— — — — ″ + NaOEt.

and the results obtained with 2-thiobarbituric acid and 2-thio-1 : 3-diphenylbarbituric acid are shown in Figs. 5 and 6. The spectrum of the former presents a series of bands similar to those given by barbituric acid, whereas the diphenyl thio-analogue shows the simplification of absorption due, as already recorded, to the introduction of phenyl radicals. In the spectra of the thio-acids, however, the bands are all moved towards the visible region, as the following values show. In 2-thio-1 : 3-diphenylbarbituric acid, the band of frequency 1/λ 3460 approximately corresponds with the band 1/λ 3760 of 1 : 3-diphenylbarbituric acid, and the bands of 2-thiobarbituric acid with approximate frequencies 1/λ 2980,

FIG. 5. FIG. 6.

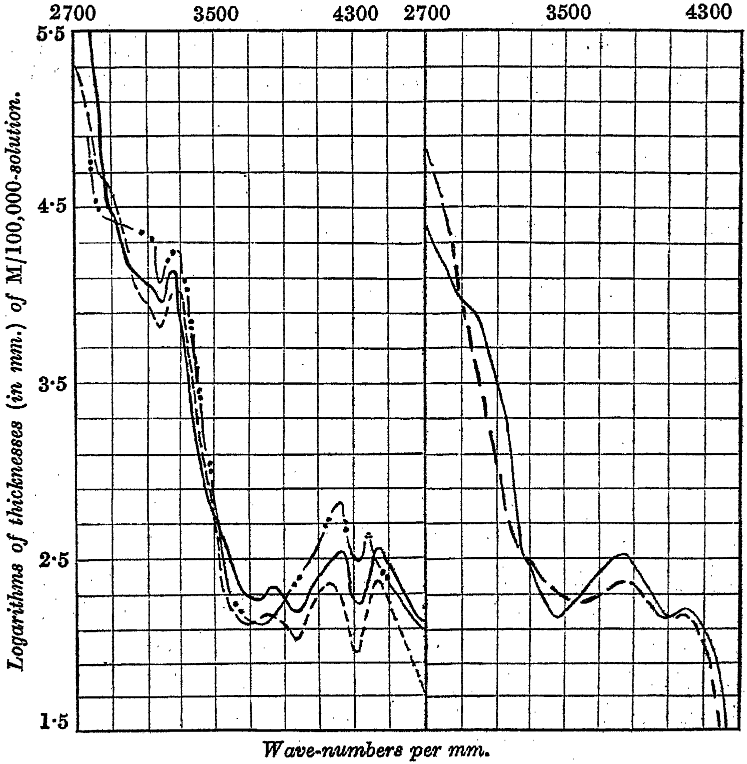


FIG. 5.

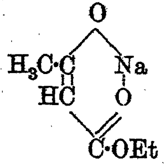
——————— 2-*Thiobarbituric acid (in water).
— — — — ,, + NaOH.
—·—··— ,, + HCl.

FIG. 6.

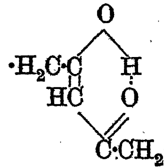
——————— 2-*Thio*-1 : 3-*diphenylbarbituric acid (in alcohol).*
— — — — ,, + NaOEt.

3550, 3760, 4120 correspond with those at 1/λ 3180, 3750, 3900, 4500 approximately in the absorption spectrum of barbituric acid. It would further appear that the enolic modifications of the thio-acids are very stable, as but little change takes place in the character of the absorption in the presence of acid.

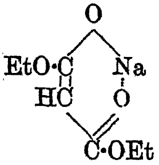
Hartley (J., 1905, **87**, 1796) reported that barbituric acid transmitted a continuous spectrum through thicknesses of *M*/1000-solution up to 20 mm. This statement is surprising, as it has been found (Brannigan, Macbeth, and Stewart, J., 1913, **103**, 406) that the sodium derivatives of malonic esters, like the metallic derivatives of ethyl acetoacetate (Baly and Desch, J., 1904, **85**, 1029; 1905, **87**, 766; Hantzsch, *Ber.*, 1910, **43**, 3049), are characterised by a deep band, and further, that 1 : 1-dimethyl*cyclo*hexane- and *cyclo*hexane*spirocyclo*hexane-3 : 5-diones and their monohalogen derivatives show (Graham and Macbeth, J., 1922, **121**, 2601) strong selective absorptions which are practically identical with the absorptions of their respective sodium salts. The hypothesis proposed (Hantzsch, *loc. cit.*; Graham and Macbeth, *loc. cit.*) to account for the selective effects in these cases is also applicable to the salts of the barbituric acids and their monohalogen derivatives, and to the acids themselves if strongly ionised, for the same type of six-membered "ring" may be produced in all cases by the formation of an internal salt calling into play auxiliary valencies of the metallic (or hydrogen) atom. It was therefore of interest to find that the apparently exceptional behaviour of the barbituric acids was due to an incorrect observation.



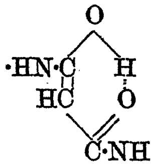
I. Sodium derivative of ethyl acetoacetate.



II. 3 : 5-Dione compounds and their salts.



III. Sodium derivative of malonic ester.



IV. Barbituric acids and their salts.

Trubsbach (*Z. physikal. Chem.*, 1895, **16**, 711) and Hantzsch (*Ber.*, 1902, **35**, 1006) traced the acidity of barbituric acid to enolisation involving the methylene group, and Wood and Anderson (J., 1906, **89**, 1831) supported this view by showing the almost negligible values of the dissociation constants of *C*-dialkyl barbituric acids compared with the value for the parent compound. It was thought that a series of conductivity measurements would afford confirmatory evidence of the enolic constitutions of the barbituric acids and their monohalogen derivatives and of the existence of the dihalogen compounds in ketonic forms. The method was applied to such substances and also to a series of derivatives of 1 : 1-dimethyl*cyclo*hexane- and *cyclo*hexane*spirocyclo*hexane-3 : 5-diones. Approximate measurements of the hydrogen-ion concentrations of the solutions were in some cases made by the capillator method.

TABLE I.

	$M/100$ in 80% alcohol.	$M/200$ in 40% alcohol.	
	A.	*A*.	*B*.
1 : 1-Dimethyl*cyclo*hexane-3 : 5-dione and derivatives.			
Parent	0·3884	2·792	3·8
4-Bromo-derivative	2·3017	22·590	2·9
4-Chloro-derivative	2·3400	21·310	2·8
4 : 4-Dichloro-derivative	0·1501	0·976	4·2
4 : 4-Dibromo-derivative	0·1694	1·222	4·1
4-Chloro-4-bromo-derivative	0·1953	1·728	4·0
*cyclo*Hexane*spirocyclo*hexane-3 : 5-dione and derivatives.			
Parent	0·4602	2·341	3·9
4-Bromo-derivative	2·3173	21·730	2·8
4 : 4-Dichloro-derivative	0·2148	0·9615	4·2

Columns *A* give the molecular conductivities at 25°, column *B* gives the hydrogen-ion concentrations.

The conductivity measurements were made with unplatinised electrodes. The figures for the molecular conductivities of the dihalogen compounds are not absolute, but maximum, values. This is due to the partial reduction of these compounds to the monohalogen compounds, which occurs on keeping. Direct tests showed that oxidation of the alcohol to aldehyde occurs with the formation of free halogen acid. The change is surprisingly rapid in the presence of platinised electrodes, and it was found possible to reduce the error to a minimum only by using unplatinised electrodes and determining the conductivity as rapidly as possible after making the solution. It is impossible to eliminate the error altogether, as the initial increase in conductivity is very rapid, and the values for the dihalogen compounds are so small that the formation of even traces of the halogen acid and monohalogen compound causes a very considerable percentage increase in the value. A typical effect of the decomposition on the conductivity values is seen in Table II, where the " molecular conductivity " (P) is the value

$$P = scx/R(1000 - x),$$

s being the cell constant, c the number of c.c. containing 1 g.-mol. of substance, R the resistance balanced against the resistance of the cell, and x the balancing length on a 1000-cm. bridge.

The values in Table I show that whereas the introduction of a single halogen atom in the 4-methylene group increases the molecular conductivity considerably, the substitution of halogen for the remaining hydrogen causes a decrease to a value considerably smaller than that of the parent compound; moreover, for the reasons stated, the experimental values for the dihalogen compounds must be considerably greater than the absolute values. It must be inferred, therefore, that whilst in the monohalogen compounds enolisation

TABLE II.

Derivatives of 1 : 1-*dimethyl*cyclo*hexane*-3 : 5-*dione*. *M*/100-*Solution in* 80% *ethyl alcohol.*

	P.		
Time (mins.).	4 : 4-Dichloro-.	4 : 4-Chlorobromo-.	4 : 4-Dibromo-.
0	0·1501	0·1953	0·1694
5	0·1968	0·2937	0·2776
10	0·2209	0·3715	0·3434
15	0·2484	0·4272	0·4085
20	0·2646	0·4679	0·4559
30	0·3135	0·5504	0·5362
45	—	0·6521	0·7205
60	0·4271	0·7439	0·9980

is greatly increased, in the dihalogen compounds the reverse obtains and the diketonic structure indicated by the absorption spectra of the compounds is supported.

Similar considerations hold good for the barbituric acids examined :

	M/100 in water.		*M*/200 in water.		*M*/1000 in water.	
Acid.	*A*.	*B*.	*A*.	*B*.	*A*.	*B*.
Barbituric	31·463	3·1	50·468	3·5	104·3	3·7
Dibromobarbituric ...	6·710	3·8	9·3305	3·9	20·28	4·0

	M/500 in 50% alcohol.	*M*/1000 in 25% alcohol.
	A.	*A*.
1-Phenylbarbituric	31·210	80·517
1-Phenylbromobarbituric ...	34·904	68·117
1-Phenyldibromobarbituric ...	3·450	9·242

A = molecular conductivity; *B* = hydrogen-ion concentration.

One of us (W. B. O.) expresses his indebtedness to the Department of Scientific and Industrial Research for a grant which enabled him to participate in the work.

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[*Received, January 24th*, 1927.]

CIX.—*The Properties of the Chlorides of Sulphur. Part I. Freezing Points.*

By THOMAS MARTIN LOWRY, LAURENCE PATRICK MCHATTON, and GRIFFITH GLYN JONES.

THE fact that the chlorination of sulphur takes place in two stages, giving rise first to an orange and then to a red product, was recorded by Berthollet in 1807. It was confirmed in 1832 by Dumas, who analysed the two products and showed that the composition and vapour density of liquids which were saturated with sulphur and with chlorine respectively agreed with those calculated for compounds of the formulæ S_2Cl_2 and SCl_2. The view has, however, been held persistently (*e.g.*, by Rose in 1831, on account of the variable composition of the red product, by Isambert in 1878, on account of its variable vapour pressure, and by Ogier in 1883, on account of its small heat of formation) that the "dichloride" does not exist as a definite chemical compound, but is merely a solution of chlorine in the monochloride. In recent years, the existence of a higher chloride of sulphur has been generally admitted; but it has been agreed almost universally that this higher chloride (which Dumas had shown to behave towards indigo quite differently from free chlorine) must be regarded as a tetrachloride, the so-called "dichloride" being merely a mixture of sulphur tetrachloride with monochloride. This conclusion is based upon cryoscopic experiments of Ruff and Fischer (*Ber.*, 1903, **36**, 418) and of Aten (*Z. physikal. Chem.*, 1906, **54**, 55, where a full bibliography is given), which showed a sharp maximum in the melting-point curve at −80°, corresponding with the crystallisation of the *monochloride*, and a rounded maximum at −30°, corresponding with the crystallisation of the *tetrachloride*, but no discontinuity which would indicate the crystallisation of a *dichloride*, although Beckmann subsequently froze out a product of this composition (*Z. physikal. Chem.*, 1909, **65**, 289).

Aten found this result particularly puzzling, since his observations of vapour pressure and boiling point proved clearly that the composition of the liquid and vapour phases, which became almost identical at the composition of the *monochloride* (but diverged widely on either side of this composition as a result of the very unequal vapour pressures of Cl_2 and S_2Cl_2, on the one hand, and of S_8 and S_2Cl_2, on the other), definitely approached one another again at the composition of the *dichloride*, provided that opportunity was given for the monochloride and chlorine to enter into chemical combination with one another; under the same conditions, however, there were only very feeble indications of any similar approach at the composition of the *tetrachloride*. Aten was therefore obliged to postulate that the equilibrium $3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4$ had a temperature coefficient which was so large that a product which was almost all SCl_2 at 0° nevertheless deposited SCl_4 at −30°.

In view of the contradictory character of the evidence, and especially of the fact that the introduction of precise physicochemical methods of examination had made the problem of the real existence of sulphur dichloride even more contentious than before, we thought it important (in spite of the obstinately negative character of the results recorded by Ruff and Fischer, and by Aten) to open up this question again, and in particular to find out whether the freezing points did in fact afford a decisive proof of the non-existence of the dichloride at low temperatures. In the present paper, therefore, we describe the results of a careful redetermination of the freezing-point curve of the chlorides of sulphur over the range from 16 to 70% Cl. This redetermination has revealed, in addition to the main sections corresponding to the separation of the *monochloride* and the *tetrachloride*, a substantial section corresponding to the crystallisation of the *dichloride*, as well as a small loop near the eutectic point, which is attributed to the crystallisation of a *trisulphur tetrachloride* of the formula S_3Cl_4, which has not been prepared before.

EXPERIMENTAL.

General Principles.—The plotting of an accurate equilibrium diagram is only possible if attention is paid to the three conditions discussed below:

(*a*) Ruff and Fischer determined the *final melting points* in sealed tubes of samples containing 51·5—92·4% Cl. In view of the tedious disturbances of equilibrium which may result from partial or complete solidification in such a complex system, we regarded it as essential to determine in every case the *initial freezing point* of the unfrozen sample. Since Beckmann's values for the m. p. and f. p. of his samples differed in some cases by as much as 40°, in spite of their theoretical identity under ideal conditions, this choice is of some importance.

(*b*) Owing to the slowness with which interaction takes place between sulphur monochloride and chlorine, Aten was able to plot b.-p. and f.-p. curves for these mixtures *before and after combination;* but it appears to have been assumed that mixtures of ready-made chlorides of sulphur come to equilibrium immediately. In our experience, this is not the case, since the f. p. of a freshly prepared mixture of sulphur monochloride and sulphur dichloride may differ by 20° from the value recorded finally. The precaution was therefore taken of heating each sample to 100° in a sealed tube in order to establish a definite condition of equilibrium before determining its f. p. It was found that identical f. p.'s were given by unheated samples to which a trace (0·02%) of iodine had been added, but not by samples which had merely been made up in presence of charcoal.

(*c*) Although both Ruff and Fischer and Aten plotted enough points to show the two maxima in the m.-p. curve, their measurements were neither numerous nor accurate enough to reveal the minor breaks in the curve. The discontinuities due to the crystallisation of sulphur dichloride and of trisulphur tetrachloride were only discovered (i) by using a triple thermo-junction, in place of pentane and toluene thermometers, and so reducing the errors of observation to less than 1°; and (ii) by plotting 15 points in a region which contained only one observation, by Ruff and Fischer, of the eutectic temperature of a sample which was not, in fact, of the eutectic composition. The m.-p. curves which had been used to prove the non-existence of the dichloride were thus shown to be wholly imaginary in the region in which this compound actually crystallises out from the melt.

Materials.—Sulphur monochloride was purified by redistillation under 30 mm. pressure from 1% each of dry charcoal and of sulphur. Liquids richer in chlorine were prepared by adding 1% of dry ignited charcoal to the purified monochloride, cooling in ice, and passing in a current of chlorine which had been dried with sulphuric acid and phosphoric oxide. Some samples were prepared by direct chlorination of the monochloride, others by mixing sulphur monochloride with an over-chlorinated sample of " dichloride " containing 70·4% of chlorine, which was kept in a stoppered bottle and analysed from time to time. The analyses were made by weighing out 0·2 g. in a stoppered glass tube, dropping the tube into a flask containing 50 c.c. of distilled water and 5 c.c. of ammonia (*d* 0·880), and boiling for 5 minutes; 10 c.c. of nitric acid (*d* 1·42) were added to the cold solution, which was boiled to remove oxides of nitrogen. After adding 50 c.c. of $N/10$-silver nitrate, and filtering off the precipitated silver chloride, the excess of silver was titrated with $N/10$-potassium thiocyanate with ferric alum as indicator. This method, which gave results agreeing within 0·1%, was found to be much more convenient than Carius's method, and at least equally accurate.

Measurement of Temperature.—The f. p.'s were measured with a triple thermo-couple made from sleeved and silk-covered copper and constantan wire, gauge 32. The junctions were silver-soldered, filed down as much as possible, and enclosed in drawn-out glass tubes; the leads were protected with shellac. The thermo-couples were calibrated at the f. p.'s of water, mercury, chlorine, and ethylene; but the parabolic relation between *E.M.F.* and temperature, which was deduced from these four readings, was checked by observing also the f. p. of hydrogen chloride, and the b. p.'s of chlorine, hydrogen chloride, and ethylene. The temperatures thus recorded were consistent within 0·5°.

Determination of Freezing Points.—The f. p.'s were determined by cooling the sample over liquid air in a test-tube; this was provided with a glass stirrer passing through a closely-fitting glass tube mounted in a cork, which also carried the thermo-couple.

The voltage did not vary with the position of the thermo-couple in the liquid, but this was kept constant in order to secure as much uniformity as possible. The liquid was cooled rapidly to within a few degrees of the expected f. p., and then by half-degrees at intervals of about a minute until solid began to separate. Samples containing *more* than the eutectic proportion of chlorine gave, within 1° from the first separation of solid, an opaque turbidity; the temperature at which this turbidity first appeared was taken as the initial f. p. of the sample; the observation was repeated twice after allowing the turbidity to clear. The turbidity in samples containing *less* than the eutectic proportion of chlorine appeared very irregularly, apparently by reason of the separation of a second liquid phase; concordant f. p.'s were observed, however, when crystallisation was induced by inoculation with a glass rod dipped alternately into the sample and into liquid air. Since there was much overcooling, the temperature at which this crystallisation could be induced *without producing a rise of temperature* was taken as the initial f. p. of the sample.

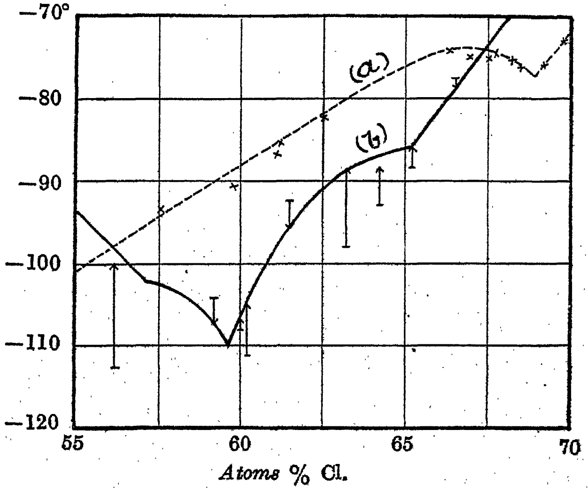
Experimental Results.

(a) *Freezing Points of Freshly Prepared Mixtures of Sulphur Monochloride and Sulphur Dichloride.*—The broken curve of Fig. 1 (*a*) shows the initial f. p.'s of a series of freshly prepared mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride, which had been prepared in presence of charcoal as described above, and contained 68·2 atoms % Cl; three points are also plotted for the same sample of dichloride after further addition of chlorine. Since all these f. p.'s fell to lower values after the mixture had been "aged" for a month in a sealed tube, and still more after heating to 100°, the curve has been drawn through the highest points, lower values being attributed to an approach towards the f. p.'s of the true equilibrium-mixtures.

The curve thus plotted differed from all others hitherto recorded in showing a pronounced maximum at the composition of sulphur dichloride, the real existence of which was thus fully established for the first time by means of f.-p. data. In spite of its very definite character, however, we do not wish to attach any undue value to this curve, since it represents only a particular series of "false equilibria," in which the interaction between the various components of the mixtures is still far from complete. The lower portion of the curve, where the f. p.'s fell below $-100°$, was regarded as untrustworthy, on account of a tendency for a second liquid phase to separate from the melt in this region, and has therefore been omitted.

(b) *Effect of Preliminary Heating on the Freezing Point of Freshly Prepared Samples.*—The samples used for plotting the f.-p. curve of Fig. 1 (*a*) did not give satisfactory values for the f. p.'s of the final equilibrium-mixtures, perhaps because the repeated manipulation of the samples had allowed too many opportunities for access of moisture. An attempt was therefore made to plot this curve by observing the f. p.'s of mixtures that had been freshly prepared *in presence of charcoal* by the direct chlorination of a sample of sulphur monochloride, under conditions which precluded the access of moisture. The f. p.'s were, however, still quite irregular, until these mixtures also had been heated to 100° in sealed tubes. The way in which the f. p.'s of the freshly prepared samples were displaced towards a smooth equilibrium curve by a preliminary heating is shown by the arrows of Fig. 1 (*b*). Although the equilibrium curve is not quite identical with that which was finally plotted, it will be seen that all the f. p.'s approach this curve, whether they were initially above it or below it, although they do not quite reach it in every case. Heating the mixtures *alone* to 100° is therefore far more efficient in producing a condition of equilibrium than mere contact *with charcoal* at atmospheric temperature.

FIG. 1.



(a) *Freezing points of freshly prepared mixtures of sulphur monochloride with sulphur "dichloride" containing* 70·4% *Cl (broken curve).* (b) *Effect of heating to* 100° *on sulphur monochloride chlorinated in presence of charcoal (full curve and arrows).*

(c) *Influence of Iodine as a Catalyst.*—Since 0·2% of iodine can be used instead of 1% of charcoal as a catalyst to promote the addition of chlorine to sulphur monochloride, experiments were made on the f. p.'s of heated mixtures to which a trace of iodine (0·02%) had been added, the proportion used being sufficiently minute to avoid the deposition of iodine trichloride on cooling. The results were as follows:

Cl =	68·4	63·1	67·3	68·0	62·2	67·6%.
=	66·1	60·7	65·0	65·7	59·8	65·3 atoms%.
F.p. =	−79·0°	−99·0°	−83·0°	−84·5°	−103·0°	−83·0° (without iodine).
=	−79·0	−98·0	−82·5	−83·5	−103·5	−83·0 (with 0·02% iodine).

No further change of f. p. was produced by the addition of iodine to the heated samples; moreover, identical values were observed when the f. p.'s of unheated samples to which iodine had been added were compared with those of samples (containing no iodine) which had been heated to 100°. It therefore appears that the condition of equilibrium brought about by the addition of iodine at atmospheric temperature is substantially identical with that produced by heating to 100°.

(d) *Freezing-point Curve of Samples previously heated to* 100°.—When a precise method for measuring the f. p.'s had been established, and a satisfactory process had been devised for bringing the sample to a uniform condition, no difficulty was experienced in plotting a f.-p. curve (Fig. 2) in which all the minor details were clearly displayed. The data from which this curve was plotted were as follows:

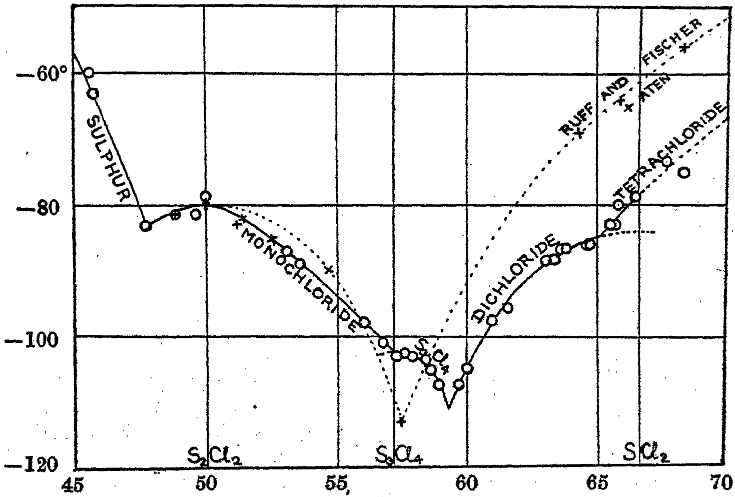
Cl %.	Atoms %.	F. p.	Cl %.	Atoms %.	F. p.	Cl %.	Atoms %.	F. p.
50·2	47·7	− 83·1°	60·9	58·4	−103·6°	66·3	63·9	−86·6°
51·6	49·1	− 81·5	61·0	58·6	−105·1	66·4	64·0	−87·2
52·1	49·6	− 81·3	61·3	58·9	−107·4	67·1	64·8	−85·9
52·5	50·0	− 79·0	62·1	59·7	−107·4	67·2	64·9	−86·1
55·6	53·1	− 87·0	62·4	60·0	−105·0	67·9	65·6	−82·9
56·1	53·6	− 89·0	63·4	61·0	− 97·6	68·2	65·9	−82·9
58·6	56·1	− 98·4	64·0	61·6	− 95·7	68·2	65·9	−80·0
59·3	56·8	−101·0	65·5	63·1	− 88·6	68·8	66·5	−78·8
59·8	57·3	−103·0	65·5	63·1	− 88·4	70·1	67·8	−73·5
60·1	57·6	−102·6	65·8	63·4	− 88·3	70·6	68·3	−75·0.
60·4	57·9	−103·0						

It will be seen that, whereas the broken curve of Fig. 1 (*a*) shows a maximum corresponding with the composition SCl_2, this is not reached in mixtures which had been brought to a condition of equilibrium by heating to 100°, since, after this treatment, *a mixture having the composition of sulphur dichloride deposits crystals of sulphur tetrachloride.*

(e) *Solubility of Sulphur in Sulphur Monochloride.*—In order to carry the equilibrium diagram up to 100% S, measurements were made of the solubility of sulphur in sulphur monochloride. For this purpose sulphur, purified by recrystallisation from toluene, was added to the monochloride, and heated to a temperature just below the transition point at 96°. The temperatures at which solid sulphur began to separate on cooling the solutions are shown with sufficient exactness in Fig. 3, which covers a much wider range of temperatures than the preceding figures. The temperatures recorded by Aten *for complete dissolution* of sulphur in sulphur monochloride are also shown; as might perhaps be expected, these are considerably higher, since complete saturation is very difficult to attain in presence of a vanishing quantity of the solid phase. It should be noted that, after being heated to 170°, sulphur dissolves permanently in sulphur monochloride, perhaps as the result of the formation of sub-chlorides of sulphur (Ruff and Golla, *Z. anorg. Chem.*, 1924, **138**, 17, 33; Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, [v], 28, 217), but there is no reason to suppose that this takes place during a short heating at temperatures below 100°.

FIG. 2.

Freezing points of chlorides of sulphur after heating to 100°.



(f) *Appearance of the Solid Phase.*—The fact that several different compounds may separate in the range from S_2Cl_2 to SCl_4 was confirmed by noting the physical appearance of the solids. Thus:

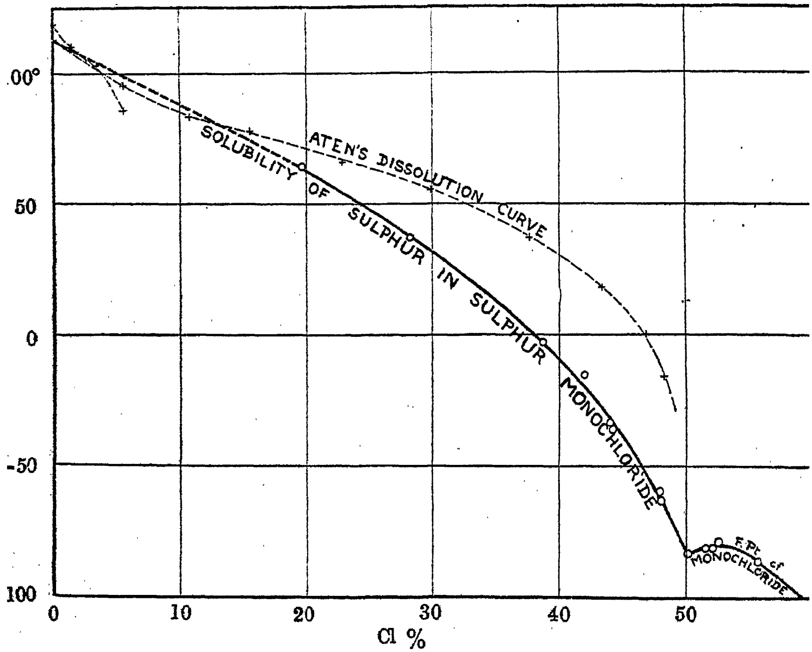
(i) *Sulphur tetrachloride* separated in a buttery form (without overcooling) from mixtures containing more than 67·2% Cl (64·9 atoms %).

(ii) *Sulphur dichloride* separated, again without overcooling, in the form of a finely divided, buff-yellow powder, from mixtures containing 61·6—67·2% Cl (59·2—64·9 atoms %).

(iii) The solid which separated over the narrow range 59·1—61·6% Cl (56·6—59·2 atoms %), after seeding with a sample cooled in liquid air in order to prevent the separation of a liquid phase, was of a flocculent nature, very different from the granular monochloride or the pasty dichloride; since this different appearance corresponded with the limits of a section of the broken f.-p. curve, it was regarded as evidence of the separation of a compound intermediate in composition between the monochloride and the dichloride.

FIG. 3.

Solubility of sulphur in sulphur monochloride.



(iv) Finally, *sulphur monochloride* separated in the usual granular form from mixtures containing less than 59·1% Cl (56·6 atoms %), although these liquids had still to be seeded in order to obtain the true f. p. of the sample.

(g) *Recrystallisation of Sulphur Dichloride.*—Although an equilibrium mixture having the composition of sulphur dichloride deposits crystals of the tetrachloride on cooling, the dichloride forms the solid phase when an over-chlorinated sample of sulphur dichloride is brought back to the correct composition by the addition of sulphur monochloride. Two samples prepared in this way were cooled over liquid air until about one-third frozen; the liquid was then decanted, and the solid remelted and again partly frozen. On analysis, the final products from a sample containing 69·4% Cl gave Cl = 68·4, 67·3 (calc., 68·9). These results are, of course, merely negative, since they only show that there was no marked change of composition on freezing; but they are of value in that they do not exhibit the striking changes of composition which would be expected if the solid phase were the tetrachloride and not the dichloride. More definite results were obtained by recrystallising the dichloride from light petroleum (b. p. 40°; f. p. −147°). The crystals which separated were drained on an asbestos filter, pressed down with the flattened end of a glass rod, and again drained from the melt. Since the solid always retained some of the solvent, the chlorine and sulphur were both estimated and the percentage composition calculated from the ratio [Found: Cl, (*a*) 68·5, (*b*) 68·0; S, (*a*) 31·5, (*b*) 32·0. SCl_2 requires Cl, 68·9; S, 31·1%].

Discussion.

The equilibrium of the chlorides of sulphur in the middle regions of concentration appears to be dominated by two simultaneous dissociations of sulphur dichloride, proceeding with very unequal speeds:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2; \quad 3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4.$$

(i) Since the combination of sulphur monochloride and chlorine is extremely slow at atmospheric temperatures, the first dissociation is probably also slow; the chlorination is, however, known to be catalysed by sulphur tetrachloride, which must therefore also act as a catalyst for the dissociation.

(ii) On the other hand, since sulphur tetrachloride acts as a carrier of chlorine in the chlorination of sulphur monochloride, its interaction with that compound is probably very rapid even at low temperatures (compare $SCl_2 + Cl_2 \rightleftharpoons SCl_4$ which takes place immediately at −75°); moreover, since the dissociation of the dichloride proceeds so far that sulphur tetrachloride actually separates as the solid phase on freezing, this reverse process evidently proceeds with similar speed, so that the second dissociation must be quite rapid.

On this simple basis, we can explain the anomalies now recorded in the f. p.'s of the chlorides of sulphur. In particular, the fact that *sulphur dichloride* separates as the solid phase from a freshly prepared mixture of two liquids, which deposit *sulphur monochloride* and *sulphur tetrachloride* respectively when frozen, is a clear indication that a large yield of the dichloride must have been produced by a rapid interaction of these two compounds, thus:

$S_2Cl_2 + SCl_4 = 3SCl_2$. Moreover, since the f. p., after rising when the two chlorides are mixed, falls again after they have aged, it is clear that the *rapid* reaction by which sulphur dichloride is *produced*, is followed by a *slow* reaction by which it is *destroyed*. This destruction probably depends on a slow dissociation of the excess of sulphur dichloride into monochloride and chlorine according to the equation $2SCl_2 = S_2Cl_2 + Cl_2$; but we are not in a position to assert that this simple and very plausible explanation is in fact correct.

Summary.

(*a*) Samples of sulphur chloride, which have been heated to 100° in sealed tubes in order to bring about a condition of equilibrium, give a f.-p. curve which exhibits not only the familiar maxima due to the crystallisation of S_2Cl_2 and SCl_4, but also two well-defined breaks which are attributed to the crystallisation of SCl_2 and of a *trisulphur tetrachloride*, S_3Cl_4, which has not been prepared previously. The molecular structure of these compounds will be discussed in a subsequent paper.

(*b*) Although an equilibrium mixture having the composition of sulphur dichloride deposits sulphur tetrachloride on freezing, freshly prepared mixtures of sulphur monochloride with an overchlorinated sample of sulphur dichloride exhibit a maximum f. p. at the composition SCl_2, which disappears when the mixture is brought to a condition of equilibrium. This is attributed to a rapid production of sulphur dichloride, followed by a slower process of destruction, perhaps $S_2Cl_2 + SCl_4 = 3SCl_2$ and $2SCl_2 = S_2Cl_2 + Cl_2$.

(*c*) Sulphur dichloride has been frozen out from mixtures freshly prepared as under (*b*), and has been recrystallised from light petroleum by cooling the solution with liquid air.

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[*Received, February* 10*th*, 1927.]

CX.—*Acid and Salt Effects in Catalysed Reactions. Part VII. The Tridimensional Co-ordination of Catalytic Variables. Relations between the Data for Pure Acids and the Corresponding Minimum-Velocity Mixtures.*

By HARRY MEDFORTH DAWSON.

IT was shown previously (Dawson, this vol., p. 213) that the reaction velocity (*u*) attributable to the action of the hydrogen and acid ions in solutions which contain an acid–salt mixture of the type cHA + xMA (c constant, x variable) is connected with the hydrogen-ion concentration by an equation which may be written

$$u = u_i(n + 1/n)/2 = u_i([H^+]/[H^+]_i + [H^+]_i/[H^+])/2 = u_i(10^{\Delta p_H} + 10^{-\Delta p_H})/2 \quad . \quad . \quad . \quad (1)$$

where n is the reduced hydrogen-ion concentration, $[H^+]_i$ and u_i are respectively the hydrogen-ion concentration and the ionic reaction velocity characteristic of the minimum-velocity mixture having the same acid concentration, and $\Delta p_H = \log_{10}n$ is the reduced p_H value of the solution in question.

Since $[H^+]_i$ and u_i vary with the concentration of the acid, the complete representation of the catalytic relations for all possible mixtures of an acid and its salts involves the tridimensional co-ordination of ionic reaction velocity, hydrogen-ion concentration, and concentration of the acid.

If the velocity and p_H co-ordinates (Dawson and Dean, J., 1926, 2872) are combined with a third on which the acid is measured directly by its molar concentration, we obtain a u–p_H–c catalytic model which consists essentially of a catenary surface. Sections parallel to the u–p_H plane give simple catenary curves. The projection on the u–c plane of the points which correspond with a fixed value of n, *i.e.*, with the same reduced hydrogen-ion concentration, gives a series of parabolic curves, as may be seen by writing equation (1) in the form

$$u = \sqrt{(k_h - k_m)k_aKc}\,.\,(n+1/n)$$

for, according to this, the ionic reaction velocity is directly proportional to the square root of the acid concentration.

The corresponding projection on the p_H–c plane gives curves of an exponential type, for, since $[H^+] = n[H^+]_i = n\sqrt{k_aKc/(k_h - k_m)}$, it follows that

$$p_H = \tfrac{1}{2}\log(k_h - k_m)/k_aK - \log n - \tfrac{1}{2}\log c$$
$$= \text{constant} - \tfrac{1}{2}\log c.$$

If the co-ordinates u, p_H, and c are replaced by log u, p_H, and log c, the loci of points corresponding with the same reduced hydrogen-ion concentration will be represented by straight lines in both the log u–log c and the p_H–log c planes. For the relations in the log u–p_H plane, we obtain from equation (1)

$$\log u = \log u_i/2 + \log(n + 1/n) \quad . \quad . \quad . \quad (1\text{A})$$
$$\text{or } \log u = \log u_i + \log\cosh\log_e[H^+]/[H^+]_i$$

which is by no means a simple curve for hydrogen-ion concentrations which are not far removed from that which characterises the minimum-velocity mixture, *i.e.*, for values of n lying between

10 and 0·1. On the other hand, it may be noted that for larger and smaller values of n, equation (1A) becomes

$$\log u = \log u_i/2 \pm \log n \quad . \quad . \quad . \quad . \quad . \quad (1\text{B})$$

which represents a pair of straight lines, which are inclined to the p_{H} axis at an angle of 45° and intersect at a point for which the ordinate is represented by $\log u_i/2$. These straight lines obviously correspond with conditions in which the catalytic effect is determined almost entirely by the hydrogen ion, on the one hand, or by the acid ion, on the other.

In some recent experiments on ester hydrolysis in buffer solutions, Karlsson (*Z. anorg. Chem.*, 1925, **145**, 1) has investigated the dependence of the rate on the value of p_{H}. By plotting empirically the logarithm of the measured velocity coefficient against p_{H}, he obtains two symmetrically disposed straight lines as the locus of his experimental points provided that these are not closer to the minimum than about 0·7 p_{H} unit. The fact that the point of intersection of these lines does not correspond with the result indicated by equation (1B) is in all probability due to the circumstance that Karlsson has omitted to take account of the catalytic effects which are produced by the constituents of the buffer solutions other than the hydrogen and hydroxyl ions.

In view of the desirability of including the entire series of p_{H} values, it seems probable that the most convenient space model for the representation of catalytic relations is that afforded by the use of the co-ordinates u, p_{H} and c. A model of this kind is illustrated in the accompanying diagram, which has been constructed from data for c values lying between 0·01 and 0·36 N and therefore falling within the range of acid concentrations for which the catalytic effect of acetic acid–sodium acetate mixtures in the acetone–iodine reaction has been actually investigated. The u and p_{H} axes are in the plane of the paper and the c axis runs from front to back.

In explanation of the model, it should be pointed out that the catenary surface has a definite boundary on the left-hand side. For a given acid concentration, the catenary cross-section terminates at a point which corresponds with the salt-free solution of the acid. Such points for $c = 0·01$ and $c = 0·04$ are indicated on the photograph by $(u_0)_{.01}$ and $(u_0)_{.04}$, respectively. The projection of these terminal points on the u–p_{H} plane gives an exponential curve corresponding with the equation

$$u_0 = (k_h + k_a - k_m)10^{-p_{\text{H}}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the u–c plane, the projection is represented by a parabolic curve.

The model suggests that the catenaries become narrower as

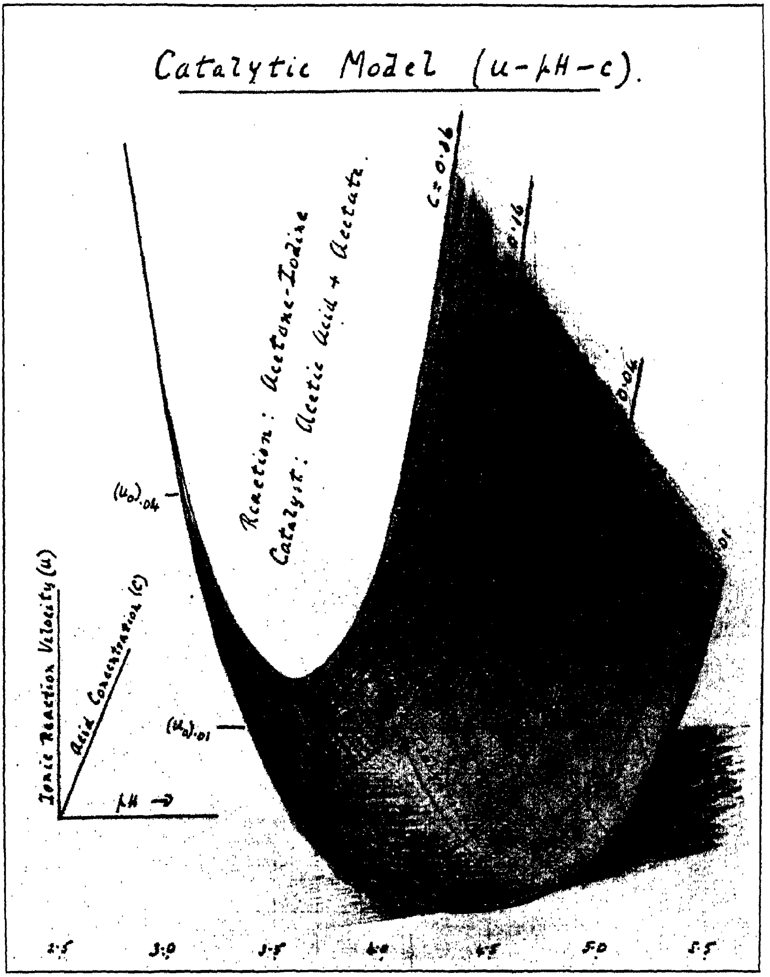


Illustration of the connexion between catalytic activity, acid concentration, and p_H *value.*

[*To face page* 758.]

the concentration of the acid increases. This is true in a certain sense, but it should be noted that the breadth of each catenary at the level of its terminal point on the pure acid side is the same for all catenary cross-sections in that this breadth is measured by $2 \log n_0$, where n_0 depends on the nature of the acid but is independent of its concentration. It has been shown in fact (Dawson, *loc. cit.*, p. 217) that both $n_0 = [H^+]_0/[H^+]_i$ and $r_0 = u_0/u_i$ are independent of c, and since $u_i = 2\sqrt{(k_h - k_m)k_aKc}$, it follows that $u_0 - u_i$ will increase with c and therefore that the catenaries will become extended in the vertical direction as the concentration of the acid increases. This is clearly shown in the diagram.

The lines drawn across the catenary surface from front to back represent approximately the loci of points which have the same reduced hydrogen-ion concentration (n); such points may be described as reduced isohydric points.

To convert the u–p_H–c model into a v–p_H–c model, every point would have to be raised in the vertical direction by k_mc.

Finally, it may be noted that the space model has a definite termination in the direction of the c axis and that the limiting catenary in the $c = 0$ plane is a catenary which is characteristic of the combined effects of the hydrogen and hydroxyl ions.

Connexion between the Catalytic Constants and the Quantities n_0 and r_0.

In the previous derivation of the relations connecting $n_0 = [H^+]_0/[H^+]_i$ and $r_0 = u_0/u_i$ with the catalytic constants, it was assumed that the acid is weak and that the hydrogen-ion concentration of the pure acid solution is given by $[H^+]_0 = \sqrt{Kc}$. It is now possible to remove this restriction and to show that the relations are applicable to any acid which ionises in accordance with the mass law. For the pure acid, the reaction velocity is given by

$$v_0 = k_h[H^+]_0 + k_a[A^-]_0 + k_m(c - [H^+]_0),$$

and since $[H^+]_0 = [A^-]_0$,

$$v_0 = (k_h + k_a - k_m)[H^+]_0 + k_mc.$$

The ionic reaction velocity is therefore

$$u_0 = (k_h - k_m + k_a) . [H^+]_0 = (k_h - k_m + k_a)n_0[H^+]_i,$$

and since $$u_i = 2(k_h - k_m) . [H^+]_i$$

we obtain $$u_0/u_i = (k_h - k_m + k_a)n_0/2(k_h - k_m) \quad . \quad . \quad . \quad (3)$$

Since, further, $$u_0/u_i = (n_0 + 1/n_0)/2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it follows that

$$n_0(1 + 1/n_0^2) = n_0[1 + k_a/(k_h - k_m)]$$

whence $$n_0 = \sqrt{(k_h - k_m)/k_a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and by substitution in equation (3) or (4)

$$r_0 = u_0/u_i = (k_h - k_m + k_a)/2\sqrt{(k_h - k_m)k_a} =$$
$$[\sqrt{(k_h - k_m)/k_a} + \sqrt{k_a/(k_h - k_m)}]/2 \quad . \quad . \quad . \quad (6)$$

Equations (5) and (6) are identical with those obtained previously on a restricted basis. They will now be examined with reference to the data which have been obtained for acetic acid as catalyst in the acetone–iodine reaction.

The relevant numbers which refer to 25° and to an acetone concentration of 20 c.c. per litre are collected in Table I. The measured velocities v_0 have been obtained by Mr. A. Key for another purpose. The values of u_0 are given by $u_0 = v_0 - k_m c$. The u_i and $[H^+]_i$ values are those recorded by Dawson and Hoskins (J., 1926, 3166), and the $[H^+]_0$ values are derived from $[H^+]_0 = \sqrt{K(c - [H^+]_0)}$ with $K = 1{\cdot}85 \times 10^{-5}$.

TABLE I.

c.	$u_0 . 10^6$.	$u_0 . 10^6$.	$u_i . 10^6$.	u_0/u_i.	$[H^+]_0 . 10^4$.	$[H^+]_i . 10^4$.	$\frac{[H^+]_0}{[H^+]_i}$.
0·01	0·216	0·201	0·041	4·90	4·22	0·47	9·0
0·05	0·512	0·437	0·089	4·91	9·52	0·93	10·2
0·1	0·762	0·612	0·123	4·97	13·5	1·32	10·2
0·2	1·170	0·870	0·164	5·30	19·2	1·90	10·1
0·5	2·10	1·35	0·270	5·00	30·4	3·05	10·0
[1·0	3·25	1·75	0·44	4·0	43·0	5·90	7·3]

Except in the case of the most concentrated acid solution, which shows very markedly the disturbing effects which have been attributed to complex-ion formation, it is apparent that the constancy of the ratios $[H^+]_0/[H^+]_i$ and u_0/u_i is as good as could possibly be expected. Taking $k_h = 465 \times 10^{-6}$, $k_a = 4{\cdot}5 \times 10^{-6}$, and $k_m = 1{\cdot}5 \times 10^{-6}$, the value of u_0/u_i according to equation (6) is 5·13, whilst the value of $[H^+]_0/[H^+]_i$ according to equation (5) is 10·15. The relations between the data for the pure acid solutions and the corresponding minimum-velocity mixtures are thus in satisfactory agreement with the theory over the concentration range $c = 0{\cdot}01$ to $c = 0{\cdot}5$. It is, of course, recognised that the nature of the equations in question is such that the data for an acid for which k_h is not so large compared with k_a or k_m would furnish a more interesting test of their validity, but such data are not yet available.

Summary.

The spatial co-ordination of catalytic variables is considered and the characteristic features of a model, constructed on the basis

of ionic reaction velocity, p_H, and acid concentration co-ordinates, are described.

A general proof is given of the equations which connect the catalytic coefficients k_h, k_a, and k_m with the hydrogen-ion concentrations and the ionic reaction velocities for solutions of the pure acids and of the corresponding minimum-velocity mixtures.

The experimental data for the catalytic effects produced by acetic acid in the acetone–iodine reaction are shown to be in close agreement with these equations over the acid concentration range $c = 0{\cdot}01$ to $c = 0{\cdot}5$.

THE UNIVERSITY, LEEDS. [*Received, February* 18*th*, 1927.]

CXI.—*Photochemical Equilibrium in Nitrogen Peroxide. Part I.*

By RONALD GEORGE WREYFORD NORRISH.

IN the course of a series of photochemical investigations with different gases, it was discovered that when nitrogen peroxide is enclosed in a water-jacketed vessel and illuminated by the rays from a quartz mercury-vapour lamp, a considerable increase of pressure is developed which is too great to be attributed to the heat effect of the absorbed radiation. For instance, with a total pressure of only 8·5 mm. of nitrogen peroxide, a pressure increase of about 3·3 mm. was obtained. For higher pressures of nitrogen peroxide, this pressure increase rapidly approached a maximum constant value of about 11·45 mm.

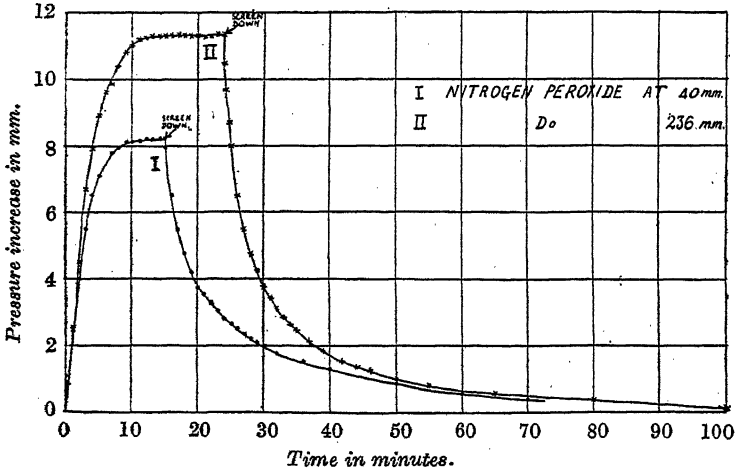
The development of this pressure under illumination started rapidly, but became slower and slower until it was complete in about 15 minutes: on being screened from the light, the gas gradually returned to its former pressure, at first rapidly and then more slowly, in the course of about 60 minutes (see Fig. 1).

It is well known that nitrogen peroxide is a mixture of two constituents, N_2O_4 and NO_2, in equilibrium with each other. The work of Bell (*Amer. Chem. J.*, 1885, **7**, 32) and of Liveing and Dewar (*Proc. Roy. Soc.*, 1889, **46**, 222) on the absorption of light by nitrogen peroxide at different pressures and temperatures leaves no doubt that the coloured constituent is the NO_2 molecule, whilst N_2O_4 (over the range of the spectrum passed by glass, at any rate) is quite non-absorbing. When the light from the mercury lamp was filtered through a plate of glass 5 mm. thick, the maximum pressure increase was only diminished by a small amount which could be partly accounted for by the loss of intensity due to reflexion at the two glass surfaces (see Part II); it was therefore concluded that the photoactive constituent of nitrogen peroxide is the NO_2 molecule. The graph of the maximum pressure increases developed in nitrogen peroxide at various total pressures is shown in Fig. 2.

It was at first thought that the pressure increase might be explained on the basis of a shift in the equilibrium $N_2O_4 \rightleftarrows 2NO_2$ under the influence of the light, but the slow recovery of the gas after the light had been shut off is in disagreement with this, since Argo (*J. Physical Chem.*, 1914, **18**, 438) has shown that the above equilibrium is attained instantaneously.

FIG. 1.

Effect of light on pressure of nitrogen peroxide.



Another possibility was that the results might be explained on the basis of the establishment of a photochemical equilibrium of the nature

$$2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2 \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

When a steady state is reached under uniform illumination, there would be an equilibrium quantity of nitric oxide and oxygen present in the system, which would recombine according to the termolecular dark reaction investigated by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 87).

In order to test this view, the effect of adding excess of nitric oxide or oxygen to the system was studied. The addition of increasing concentrations of either of these gases would throw back the photochemical equilibrium to a greater and greater extent until the increase of pressure due to photochemical equilibrium

FIG. 2.

Pressure changes in nitrogen peroxide on illumination.

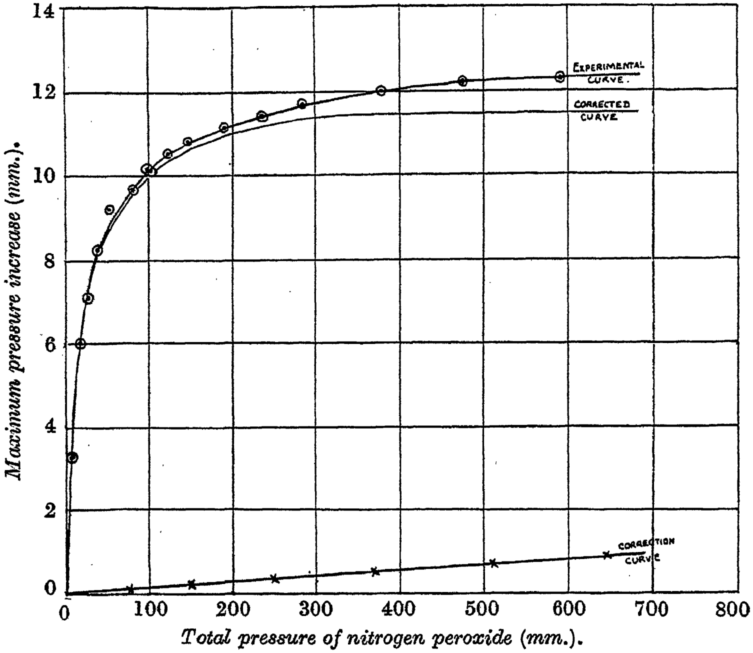
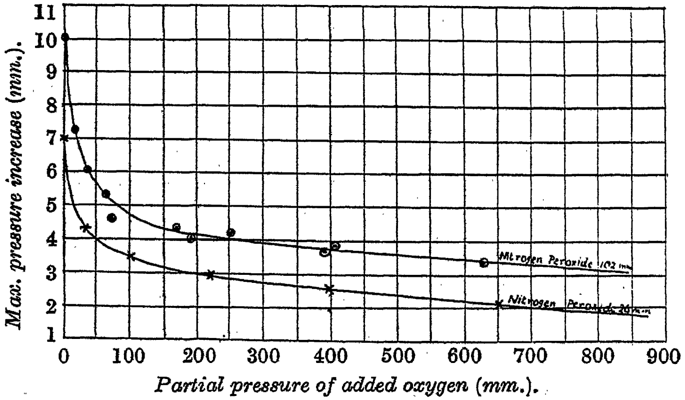


FIG. 3.

Effect of oxygen.

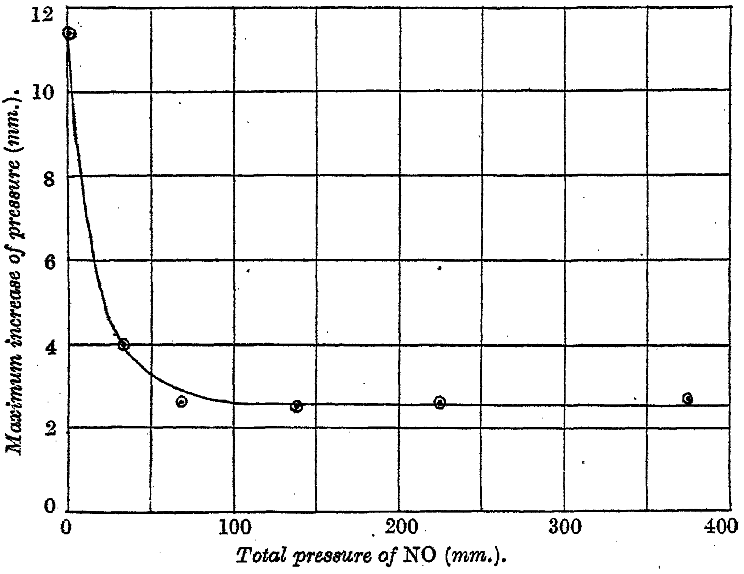


would be very small indeed. This was actually found to be the case (Figs. 3 and 4, Tables III and IV), and in accordance with the fact that the velocity of the reaction $2NO + O_2 = 2NO_2$ depends upon the square of the concentration of nitric oxide, and only on the first power of that of the oxygen, nitric oxide was found to be the more effective in displacing the equilibrium.

The experiments with excess of nitric oxide and oxygen also showed that after the photochemical equilibrium had been completely suppressed there was still a small residual pressure increase. It will be shown later that this residual effect is proportional to the total light energy absorbed by the nitrogen peroxide, and is suitably ascribed to the sum of the heat liberated by the reverse reaction $2NO + O_2 \longrightarrow 2NO_2$ and the direct heating effect of the absorbed radiation.

FIG. 4.

Effect of nitric oxide.



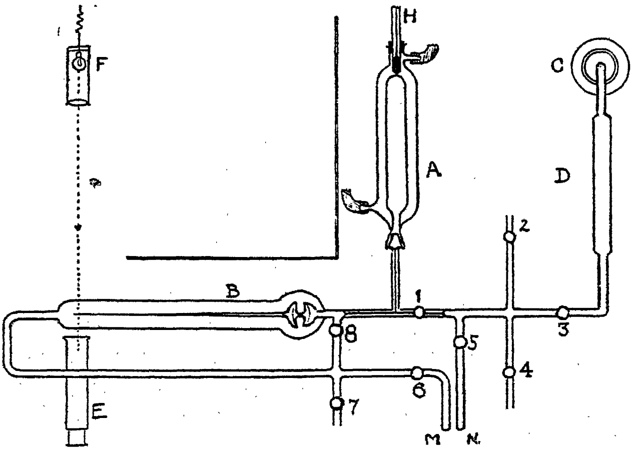
Granted that the primary photochemical reaction is a decomposition of the NO_2 molecule, the order of the reaction still requires elucidation. A unimolecular reaction would require the liberation of atomic oxygen, and seems improbable in view of the high energy required to effect this. A bimolecular reaction might take place upon the collision of an active with an inactive NO_2 molecule, with the liberation of molecular oxygen. That no atomic oxygen is liberated seems to be proved by the fact that when nitrogen peroxide was illuminated in the presence of hydrogen as a depolariser, no water was formed. The hydrogen indeed slightly decreased the pressure increase (see Table II), but this seems to be simply explained as due to the more rapid loss of heat by the system consequent upon the increased conductivity resulting from the addition of hydrogen. It may therefore, for the present, be concluded that the photochemical decomposition of nitrogen peroxide takes place by way of a bimolecular rather than a unimolecular reaction.

It is shown later that the numerical results obtained can be quantitatively explained on the basis of the above hypothesis.

EXPERIMENTAL.

The apparatus employed is shown in Fig. 5. The reaction chamber, A, a double-jacketed clear quartz vessel, was made all in one piece, and through the outer part water at a known temperature (shown by the thermometer H) could be circulated from a thermostat by a pump. The inner part of the vessel A was 18 cm. long and 3 cm. in diameter, and was joined by the ground joint to capillary tubing which communicated with the rest of the apparatus. The pressure changes were measured by the Bourdon gauge B (see Norrish, J., 1925, 127, 2316), the deflexions of the style of the gauge being observed by a low-power microscope containing a calibrated scale in the eye-piece. A maximum pressure change of about 30 mm. of mercury could be measured by this means to an accuracy of *ca.* 0·05 mm., one scale division corresponding to 0·38 mm. The gauge was surrounded by an outer jacket in which the air pressure could be varied from 0 to 1 atm., thus enabling the total pressure of nitrogen peroxide and other gases which attack mercury to be measured. To effect this the pressure in B was equalised with that in A by means of the stopcock 7, the gauge pointer being brought to zero on the scale, and the pressure of the air was obtained by reading

FIG. 5.



the vertical mercury manometer, M. By means of the stopcock 8 the pressures in the inside and outside of the gauge could be equalised rapidly, in cases of emergency, to save fracture of the gauge.

The apparatus could be evacuated by way of stopcock 4, which made connexion through calcium chloride and phosphoric oxide drying tubes to a water pump and a Toepler pump, and the pressure could, if desired, be measured directly on a vertical manometer at N.

The nitrogen peroxide after purification was stored in the bulb C, and when not in use was kept in liquid air; when required, it was allowed to melt completely by removing the liquid air, and the vapour was admitted to the evacuated reaction chamber by way of the phosphoric oxide drying tube, D, and stopcocks 3 and 1.

Through stopcocks 2 and 1 pure hydrogen, oxygen, or nitric oxide could be admitted after passing through a series of drying tubes containing calcium chloride and phosphoric oxide. The contents of the quartz vessel were illuminated by a double-barrelled quartz mercury-vapour lamp, of 3000 candle power, with a burner voltage of 150 volts, and carrying a current of 2·5 amps. The lamp was placed vertically beneath and parallel to the reaction vessel A, at a distance of 5 cms. Between the lamp and the vessel A was a horizontal brass screen which could be conveniently opened against the action of a spring by means of a cord working over pulley wheels. When the cord was released the spring automatically closed the screen. In this way, the reaction vessel could be rapidly illuminated or screened at will. A glass screen also could be placed between the reaction vessel and the lamp if desired.

In carrying out an experiment, the reaction vessel, the gauge, and the bulb C were first evacuated as completely as possible by the Toepler pump. Connexion with the pump was then cut off, the nitrogen peroxide was vaporised by the method described, and admitted to the reaction chamber to the required pressure, and stopcocks 3 and 1 were then closed. The liquid-air bath was replaced on the nitrogen peroxide bulb, and the connecting tubes between stopcocks 1, 2, 3, 4, and 5 were evacuated by means of the water pump and washed out several times with any other gas, *e.g.*, pure dry hydrogen, nitric oxide, or oxygen, which could then be admitted to the reaction vessel if required. In the meantime, the lamp had been running for about 10 minutes, in order to reach a steady rate of burning, the screen being closed. The gauge pointer being accurately adjusted to zero, an exposure was now made by opening the screen, and readings of the pressure increase were taken at intervals of about 20 secs. at first, extending to several minutes when the pressure change was completed. When the maximum pressure increase had been obtained in this way, the screen was closed, and the pressure returned slowly to its original value. It was found necessary to introduce a small and uniform correction into the readings of the pressure changes, due to a slight heating by the lamp of that part of the reaction chamber (*i.e.*, the capillary leads) which was outside the thermostat. This correction curve was determined by observations on the increase of pressure when air at different pressures was enclosed in the reaction vessel; and since the corrections could be determined as accurately as the original measurements themselves, the corrected pressures were of the accuracy (0·05 mm.) already specified. A graph of the actual readings of the pressure change in pure nitrogen peroxide is shown in Fig. 2, together with the correction curve obtained from the measurements on air. The corrected pressure changes themselves are recorded in the tables under the heading "Press. increase (obs.)."

The nitrogen peroxide was prepared by distillation of lead nitrate in a slow stream of oxygen. The evolved gas was passed through a phosphoric oxide drying tube, and condensed by means of a freezing mixture of carbon dioxide and ether. It was fractionated twice in a stream of oxygen, through drying tubes, and finally distilled into the bulb C, and attached to the apparatus (Fig. 5). When cooled in liquid air it froze to a mass of absolutely colourless crystals, which melted to a very pale yellow liquid boiling at 21·5°.

In Table I, the corrected pressure increases for the pure gas are shown; in Tables II, III, and IV, respectively, the results

TABLE I.

Pressure Change in Nitrogen Peroxide on Illumination.

Total press. of nitrogen peroxide, P.	Initial press. of NO_2, p.	Equil. press. of NO_2, p_1.	Press. increase	
			(obs.), n.	(calc.), $x + y$.
8·5	7·67	2·8	3·3	3·70
19	15·6	9·4	5·95	5·80
26	20·3	14·2	7·0	6·66
40	28·6	23·1	8·15	7·91
53	35·6	30·3	9·1	8·68
81	58·3	44·4	9·55	9·57
100	56·2	52·4	10·0	9·97
102	56·8	53·2	10·0	9·99
123	64·8	60·7	10·35	10·28
146	72·6	69·3	10·6	10·53
148	73·3	70·0	10·55	10·56
193	87·2	84·7	10·8	10·85
236	99·0	96·6	11·05	11·03
286	111·7	109·6	11·3	11·17
381	133·3	131·2	11·45	11·30
476	152·7	151·4	11·45	11·38
593	173·0	172·1	11·40	11·43

showing the effects of hydrogen, oxygen, and nitric oxide, are given. All pressures are in mm. Hg, and all the experiments were at 20°.

The results of Tables III and IV are plotted in Figs. 3 and 4. From these curves the residual pressure change, remaining after the equilibrium is completely suppressed, can be deduced as described in a later section.

TABLE II.

Effect of Hydrogen.

Nitrogen peroxide at 148 mm. pressure.

Press. of hydrogen ...	0	67·5	174	368	579
Press. increase	10·55	10·15	10·1	10·05	9·8

TABLE III.

Effect of Oxygen.

Press. of nitrogen peroxide, P.	Equil. press. of NO_2, p_1.	Initial press. of O_2.	Total press. change	
			(obs.), n.	(calc.), $x + y$.
102	53·2	0	10·0	10·0
102	54·6	17	7·25	6·92
102	55·3	36	6·05	5·76
103	56·1	64	5·3	5·00
102	55·9	73	4·55	4·85
103	56·6	169	4·35	4·02
102	56·3	191	4·0	3·91
100	55·3	254	4·2	3·68
102	56·5	394	3·69	3·44
103	56·7	409	3·85	3·43
102	56·6	631	3·35	3·22
26	13·3	0	7·0	6·56
26	17·7	33	4·3	3·64
26	18·1	101	3·45	2·66
26	18·6	221	2·9	2·21
26	18·9	399	2·55	2·00
26	19·4	655	2·1	1·84

TABLE IV.

Effect of Nitric Oxide.

Press. of nitrogen peroxide, P.	Equil. press. of NO_2, p_1.	Initial press. of NO, P_{NO}.	Total press. change	
			(obs.), n.	(calc.), $x + y$.
236	96·5	0	11·4	11·40
235	97·5	28	4·0	5·10
233	97·5	68	2·6	3·14
233	97·5	137	2·5	2·93
233	97·5	249	2·6	2·84
233	97·5	373	2·65	2·82
446	146	249	2·84	3·0
19	15·6	222	0·95	1·03

Theoretical Treatment.

In accordance with the considerations given earlier in this paper, it will now be assumed as a working hypothesis:

(1) That the NO_2 is the photoactive constituent.

(2) That the photodecomposition is bimolecular.

(3) That collision between an active and an inactive NO_2 molecule may result either in chemical change, or in the degradation of the activating energy to heat.

(4) That heat is produced both by the recombination of nitric oxide and oxygen and by the thermal degradation of the absorbed light energy.

The pressure of NO_2 present at each of the pressures used was found by the help of the equation of Wourtzel (*Compt. rend.*, 1919, **169**, 1397) for the dissociation constant of nitrogen peroxide,

$$\log K_p/T = -2810{\cdot}5/T + 8{\cdot}9908 \quad . \quad . \quad . \quad (1)$$

which gives $K_p = 71{\cdot}71$ at 20°, the unit of pressure being mm. Hg.

If P be the total pressure of N_2O_4 and NO_2, and p the partial pressure of NO_2, then, at 20°, $p^2/(P - p) = 71{\cdot}71$,

whence $$p = \sqrt{71{\cdot}71\,P + 1285} - 35{\cdot}85 \quad . \quad . \quad . \quad (2)$$

The partial pressures of NO_2 for various total pressures of nitrogen peroxide were calculated by this equation, and a curve was constructed showing the relation between p and P; from this curve the figures shown in the column headed "Initial press. of NO_2" were read off. This pressure of NO_2 present at the start of the experiments has now to be corrected to the pressure obtaining at equilibrium, which will in general be different on account of the photochemical decomposition which has taken place. The correction is relatively large at low pressures, but small at high pressures of NO_2. It is obtained as follows:

If x is the equilibrium pressure increase (exclusive of heating effect) due to the reaction (α) (p. 762), then $2x$ will indicate the equilibrium excess pressure of nitric oxide present in the system. The total nitrogen peroxide present, represented entirely as NO_2, is $2(P - p) + p = 2P - p$. When the photochemical equilibrium is established, this quantity is decreased by the amount $2x$, and if P_1 and p_1 are the new total pressure of nitrogen peroxide and partial pressure of NO_2, respectively, then

$$2P - p - 2x = 2P_1 - p_1 \quad . \quad . \quad . \quad . \quad (3)$$

Also, as before, $$p_1^2/(P_1 - p_1) = 71{\cdot}71 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whence, solving equations (3) and (4), we obtain

$$p_1 = \sqrt{71{\cdot}71P - 35{\cdot}85p - 71{\cdot}71x + 321} - 17{\cdot}93 \quad . \quad . \quad (5)$$

Equation (5) gives the pressure of the photoactive constituent, the NO_2 present when the photochemical equilibrium has been established, from the known values of P and p, and from the value of x

as obtained in a later section. The values of p_1 have been calculated and tabulated in the columns headed " Equil. press. of NO_2 " in the tables.

The Photochemical Effect.

We shall now consider the photochemical equilibrium in the nitrogen peroxide. If Y represents the equilibrium concentration of active NO_2 molecules, then their rate of formation, which is proportional to the total light absorbed by the NO_2, may be written

$$dY/dt = k_1I(1 - e^{-kp_1}) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where I is the intensity of light entering the reaction chamber, and $(1 - e^{-kp_1})$ is the fraction of the photochemically active light absorbed by the NO_2.

The active molecules, according to hypothesis, collide with inactive NO_2 molecules, and cause either thermal degradation or photochemical reaction, the respective coefficients being k_2 and k_3. Thus

$$- dY/dt = k_2Yp_1 + k_3Yp_1 \quad . \quad . \quad . \quad . \quad (7)$$

From equations (6) and (7), at equilibrium,

$$Y = k_1I(1 - e^{-kp_1})/p_1(k_2 + k_3) \quad . \quad . \quad . \quad (8)$$

The rate of photochemical decomposition is therefore

$$k_3Yp_1 = k_1k_3I(1 - e^{-kp_1})/(k_2 + k_3) \quad . \quad . \quad . \quad (9)$$

At equilibrium, this is balanced by the rate of recombination of the products, and if x is the equilibrium pressure increase, as before, and P_O and P_{NO} are the pressures of oxygen and nitric oxide initially present in the system, then the velocity of recombination, according to Bodenstein and Lindner (*loc. cit.*), will be :

$$k_4(P_O + x)(P_{NO} + 2x)^2$$

whence

$$(P_O + x)(P_{NO} + 2x)^2 = k_1k_3I(1 - e^{-kp_1})/k_4(k_2 + k_3) \quad . \quad . \quad (10)$$

So long as the light intensity remains constant, as in the present experiments, we may write $k_1k_3I/k_4(k_2 + k_3) = K$ and

$$(P_O + x)(P_{NO} + 2x)^2 = K(1 - e^{-kp_1}) \quad . \quad . \quad (11)$$

In the first series of experiments, pure nitrogen peroxide was used; P_O and P_{NO} were therefore zero, hence

$$x = \sqrt[3]{K(1 - e^{-kp_1})/4} \quad . \quad . \quad . \quad . \quad (12)$$

which gives the pressure increase due to photochemical equilibrium and exclusive of the heating effect.

The Heating Effect.

We may now obtain an expression for the heating effect. From equation (7) above, it follows that the heat evolved per second due to thermal degradation is proportional to

$$k_2Yp_1 = k_1k_2I(1 - e^{-kp_1})/(k_2 + k_3) \quad . \quad . \quad . \quad (13)$$

The heat evolved per second by the recombination of the nitric oxide and oxygen is proportional to

$$(P_O + x)(P_{NO} + 2x)^2 = K(1 - e^{-kp_1}).$$

The total heat evolved per second is therefore proportional to

$$\{k_1k_2I/(k_2 + k_3) + K\}(1 - e^{-kp_1}) = K_1(1 - e^{-kp_1}) \quad . \quad . \quad (14)$$

This heat is conducted away at a constant rate, independent of the total gas pressure, for the thermal conductivity of a gas does not vary between pressures of 1 and 760 mm. (Meyer, "Kinetic Theory of Gases"). It therefore follows that there will be a constant equilibrium excess quantity of heat, which we may represent by h, present in the system, and proportional to $K_1(1 - e^{-kp_1})$. The gas will therefore be at a slightly higher temperature than the thermostat, the temperature increment being given by

$$dT = k_5h/MC_v \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where M is the total number of moles of gas present in the vessel, and C_v the specific heat at constant volume. If v be the volume of the reaction vessel, then

$$Pv = MRT \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

whence, at constant volume,

$$v.dP = MR.dT = k_5MRh/MC_v \quad . \quad . \quad . \quad (17)$$

Therefore $\quad dP = k_5Rh/vC_v = K_0(1 - e^{-kp_1}) \quad . \quad . \quad . \quad (18)$

where $\quad K_0$ is proportional to K_1k_5R/vC_v.

The pressure increase dP due to the combined heating effect of the light and the reverse reaction is therefore proportional to the total quantity of light absorbed. We may represent it by y and write

$$y = K_0(1 - e^{-kp_1}) \quad . \quad . \quad . \quad . \quad . \quad (18\text{A})$$

Determination of the Constants of Equations (11) *and* (18).

For the evaluation of the constants of equations (11) and (18) the data in Table III were used. The total pressure increase, n, is the sum of that due to the reaction, x, and that due to the heating effects, y. With excess of oxygen present the value of the former is rapidly diminished as the photochemical equilibrium is suppressed, whilst the latter is only slightly changed, since the quantity $(1-e^{-kp_1})$, upon which y depends (equation 18A), alters only to a small extent as x approaches zero (equation 5, x being always small compared with P).

Thus, as increasing quantities of oxygen are added to a given quantity of nitrogen peroxide, the magnitude of the pressure change on illumination approaches asymptotically to the value of y. This is shown quite clearly in the experimental curves (Fig. 3).

When excess of oxygen is present, the initial pressure of nitric oxide being zero, equation (11) becomes

$$(P_0 + x)x^2 = K(1 - e^{-kp_1})/4 \quad . \quad . \quad . \quad . \quad (19)$$

Now p_1 is in general different from p, the pressure of NO_2 introduced into the bulb, on account of the photochemical decomposition which has occurred, and the small correction by which the known values of p are converted to p_1 is obtained from the observed pressure change as follows.

We take the asymptote of the oxygen curve to give y when x approaches zero (*i.e.*, when the photochemical equilibrium is completely suppressed). At this point, equation (5) reduces to $p_1 = p$, and since p is known, K_0 and k can be calculated from the asymptotic values of the two oxygen curves and the known values of p by equation (18A). By this means, using the data in Table III for nitrogen peroxide at 102 mm. and 26 mm., we find $K_0 = 3{\cdot}02$ and $k = 0{\cdot}0267$, the asymptotic values of y being taken as 2·3 mm. and 1·3 mm., respectively.

Approximate values of x required to correct p to p_1 by equation (5) can now be obtained from the observed values of the pressure change (n) by subtracting from them the asymptotic value for y used above. Actually, of course, the value of y changes slowly as x increases, but the total variation in extreme cases is not more than 10%, and the corresponding values of x are not in error by more than 2% when this single value of y is used. The values of p_1 obtained therefrom are not affected to the extent of more than 1% by this approximate treatment, and in most cases by very much less.

From the values of p_1 so obtained, and the constants K_0 and k found above, the values of y for different oxygen pressures are next calculated. These, when subtracted from the observed total pressure change, give the "accurate" observed values of x from which, on substitution in equation (19), we find $K = 2416$. The sums of the calculated values of x and y are shown in Table III and are in good agreement with the observed values for the total increase of pressure.

With excess of nitric oxide present, the photochemical equilibrium is soon almost completely suppressed, the effect being greater than that of oxygen as anticipated (p. 763). Equation (11) now becomes

$$(P_{\text{NO}} + 2x)^2 x = K(1 - e^{-kp_1}) \quad . \quad . \quad . \quad . \quad (20)$$

Calculating p_1 as before, and taking the same values for K, k, and K_0, the values of $(x + y)$ have been calculated from equations (20) and (18A) and show suitable agreement with the observed values (Table IV).

Finally, we can now test equation (12), which applies to systems containing no added nitric oxide or oxygen (Table I). Taking the values of K_0, K, and k already found, we have

$$x^3 = 604(1 - e^{-0{\cdot}0267p_1}) \quad . \quad . \quad . \quad . \quad (12\text{A})$$

and $$y = 3{\cdot}02(1 - e^{-0{\cdot}0267p_1}) \quad . \quad . \quad . \quad . \quad (18\text{B})$$

Hence $$x^3 = 200y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Also $$x + y = n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where n is the total observed pressure change. The "observed" value of x can therefore be obtained from the recorded values of n by solving equations (21) and (22), and has been used in equation (5) as before to calculate values of p_1 for the different pressures of nitrogen peroxide used. From these values using equations (12A) and (18B) the values of $(x + y)$ given in the last column of the table have been calculated. It will be seen that close agreement is obtained.

In Table V are shown the experimentally determined heat effects in the presence of excess of nitric oxide or oxygen as described above; the calculated heating effect (y) obtained from equation (18B), putting $p_1 = p$ (since x is negligibly small), is tabulated for comparison. The agreement obtained can leave no doubt that the heating effect is actually proportional to the quantity of light absorbed as is demanded by the theory.

TABLE V.

Heating Effect.

Press. of nitrogen peroxide.	Press. of NO_2 ($p_1 = p$).	Press. change due to heating. (obs.).	(calc.).
19	15·6	0·95	1·03
26	20·3	1·3	1·23
100	56·8	2·3	2·36
233	97·5	2·6	2·82
446	146	2·85	3·00

The close agreement that has been obtained between the observed and the calculated values of the pressure change of nitrogen peroxide on illumination shows that the theory of the change adopted is in agreement with the facts. It may therefore be definitely stated :

(1) That nitrogen peroxide is decomposed by the light of the mercury-vapour lamp into nitric oxide and oxygen.

(2) That a photochemical stationary state is set up resulting in an increase of pressure in the system.

(3) That the probable mechanism is, first, the activation of an NO_2 molecule, and, secondly, the reaction of this active molecule with an inactive molecule of NO_2 to produce nitric oxide and oxygen.

In Part II of this series the photo-kinetics of this change will be further investigated and discussed.

In the light of these experiments, it is now possible to understand the experiments of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72), who found that nitrogen pentoxide is apparently decomposed photochemically by blue light, but only in the presence of nitrogen peroxide, and drew from this the erroneous conclusion that the thermal decomposition of the pentoxide must also be influenced by the peroxide (Daniels, Wulf, and Karrer, *ibid.*, 1922, **44**, 2402). This was disproved by Hirst (J., 1925, **127**, 657) and later by White and Tolman (*J. Amer. Chem. Soc.*, 1925, **47**, 1240), who showed that the thermal decomposition is uninfluenced by the presence of the peroxide.

We may now assume that the photochemical decomposition of nitrogen pentoxide is a secondary dark reaction taking place according to the scheme

$$2NO_2 \xrightarrow{\text{light}} 2NO + O_2$$

$$NO + N_2O_5 \xrightarrow{\text{dark}} 3NO_2.$$

The second reaction, being bimolecular, is more likely to take place than the reverse of the first reaction, which is termolecular, so that the whole of the pentoxide will be decomposed as a result of the photodecomposition of the NO_2.

On this view, it is obvious that the mechanisms of the photochemical and thermal decompositions of nitrogen pentoxide are entirely different, and that no effect on the latter is to be expected in the presence of NO_2, in view of its effect on the former.

Summary.

It has been found that nitrogen peroxide undergoes a marked change of pressure on illumination by mercury light. This pressure change is too great to be accounted for on the basis of a heating effect due to the absorbed light, and has been found to be due (1) to

the establishment of a photochemical equilibrium in the system represented by the equation

$$2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} 2NO + O_2,$$

and (2) to a heating effect, due to the recombination of the nitric oxide and oxygen and also to the absorbed radiation.

A reaction mechanism involving reaction between active and inactive NO_2 molecules is proposed and is in quantitative agreement with the observed results.

A simple mechanism for the photodecomposition of nitrogen pentoxide is proposed.

The author desires to express his thanks to the Chemical Society for a grant which has in part defrayed the cost of the apparatus used in these experiments.

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[*Received, December 2nd,* 1926.]

CXII.—*Studies in Polymerisation. Part I.* 2:3:4-*Trimethyl* l-*Arabonolactone.*

By HARRY DUGALD KEITH DREW and WALTER NORMAN HAWORTH.

IN view of the current tendency to regard cellulose, inulin, and possibly starch and other complex polysaccharides as polymerides of anhydrohexose units (Hess and Schultze, *Annalen*, 1926, **448**, 99; H. Pringsheim, *Ber.*, 1926, **59**, 3008; M. Bergmann, *Ber.*, 1926, **59**, 2079), the communication of definite experimental evidence of the molecular association of simple derivatives of the natural sugars is of special interest.

A conspicuous example of the ease of polymerisation of a unit of this nature is furnished by our recent studies of the behaviour of 2:3:4-trimethyl *l*-arabonolactone (I). This compound, which has hitherto been obtained only in the form of a syrup, is now shown to be crystalline in the pure state (needles, m. p. 45°), and to display a specific rotation +180° in water, as compared with the former value +145° (Pryde, Hirst, and Humphreys, J., 1925, **127**, 355). The crystalline lactone is readily soluble in cold ether and in other organic solvents as well as in water. In the liquid condition, it is hygroscopic, absorbing water with great rapidity on exposure to the atmosphere; in the crystalline state, it displays this property only to a limited extent. Nevertheless, after 2 days' exposure, the crystals change to a liquid which is almost entirely the free monobasic acid. It is therefore evident that the monomeric form of the lactone, which contains a simple six-membered ring, is characterised by its high rotatory power, ready fusibility, high solubility, and by the ease with which it is hydrolysed in the presence of water vapour.

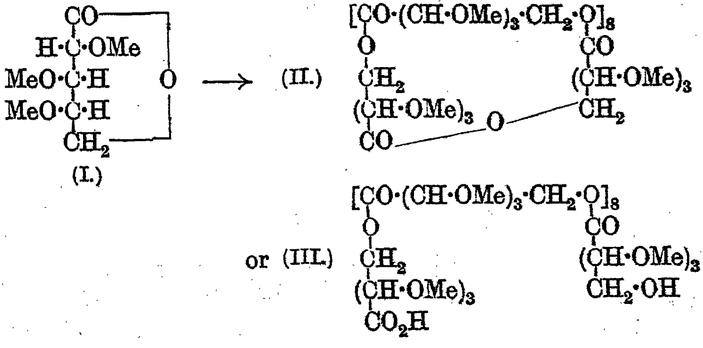
When the lactone is kept, however, for some time in an atmosphere containing traces of acetyl chloride vapour or of hydrogen chloride gas, it undergoes a remarkable change. The transformation product is a white powder which is insoluble in ether and sparingly soluble in benzene or other organic solvents. From solution in hot benzene, it separates as a white, colloidal precipitate which, on removal from the solvent, appears as a mass of microscopic, barrel-shaped crystals having a considerably higher melting point (135—138°) than the original lactone (45°). This crystalline transformation product is stable during many weeks in moist air, and the specific rotation in benzene is only about one-fifth of that of the original lactone. The analytical figures indicated that the new product possessed the same or almost the same empirical formula as the simple lactone, whilst it was shown by titration that complete transformation to the sodium derivative of the simple acid occurred after heating for 20 minutes at 100° with a slight excess of $N/10$-sodium hydroxide. With the theoretical amount of alkali this period was not sufficient to effect complete disruption of the complex, thus indicating that the latter is possessed of far greater stability than the simple lactone towards hydrolytic agents.

The foregoing evidence, particularly the behaviour towards solvents, pointed unmistakably to the identification of the compound as a polymeride of the trimethyl arabonolactone. This deduction was confirmed by determinations of molecular weight in boiling benzene, which yielded the figures 1900 ($c = 1{\cdot}05$) and 2100 ($c = 2{\cdot}25$). Moreover, it was found that the polymeride could be completely transformed to the simple crystalline lactone by heating to 175° in a vacuum, or by successive treatment with alkali and the equivalent of dilute mineral acid. Indeed, the regenerated lactone solidified even without preliminary distillation, yielding crystals, m. p. 45°, identical with the initial material. There can thus be little doubt that the polymerised product consists of a complex containing about ten associated molecules of the simple lactone $C_8H_{14}O_5$.

The important consideration arises whether the polymerisation occurs as a result of the union of the pre-formed, six-membered rings by the exercise of residual valencies, or whether structural change is responsible for the formation of a long chain or a large ring of carbon and oxygen atoms united only by principal valencies. At present there is no evidence to support the former view, whilst the properties of the polymeride appear to favour the latter hypothesis. Thus the lower specific rotation of the polymerised compound suggests the elimination of the original six-membered ring and favours the probability of a chain formula in which the lower order of rotatory power may be expected. Again, the much enhanced stability of the polymeride towards moisture would seem to indicate a profound modification of the easily ruptured ring of the initial lactone. So remarkable a change in a simple monocyclic sugar derivative of this nature is unexpected, since earlier examples of such a change have usually been furnished mainly by dicyclic compounds, such as the glucosans. Evidence of the polymerisation of the γ-derivatives of sugars has been adduced, but this has usually been indeterminate in character. We incline to attribute to the new polymeride the formula (II), symbolising a chain of some 50 carbon atoms and 11 oxygen atoms, which may be closed, or which may have the two terminal groups as shown in (III). That a ring structure such as (II) would probably be strainless is conceivable from the work of Ruzicka and his co-workers (*Helv. Chim. Acta*, 1926, 9, 499).

Analysis fails to decide with certainty between these alternatives, although it may be remarked that the analytical figures correspond more closely with the closed-chain formula (II).

Some evidence of the partial hydrolysis of the polymeride is given by its behaviour in water, in which it is very sparingly soluble in the cold. The hot aqueous solution was feebly acid to litmus, and the acidity did not increase on boiling; and the cooled solution, which deposited only a negligible quantity of the substance, showed a small lævorotation. Evaporation to dryness gave the original polymeride, apparently pure, in the form of broken prisms, m. p. 136—139°. The change to lævorotation after boiling with water may be due to the transformation of the cyclic compound (II) to the open-chain compound (III).



The existence of a crystalline polymeride of this nature, and the simple means by which it can be formed or disrupted, provide a significant commentary on the formulæ which have recently been proposed for cellulose, representing this polysaccharide as polymerised anhydro-glucose, $C_6H_{10}O_5$. Although there remains the possibility that our complex substance may be a mixture of higher polymerides giving an average molecular weight only, yet the crystalline character of the product as revealed under the microscope appears to point to its homogeneity.

EXPERIMENTAL.

2 : 3 : 4-*Trimethyl* l-*Arabonolactone*.—Crystalline trimethyl methylarabinoside (m. p. 44°) was hydrolysed by 3% hydrobromic acid, and the product oxidised at 65—70° with bromine. The *lactone*, a viscid, colourless, hygroscopic liquid ($n_D^{15 \cdot 5^\circ}$ 1·4630), very readily soluble in ether and other organic solvents, solidified to a mass of silky, prismatic needles, m. p. 45° with previous softening. After being drained on porous tile in a vacuum, the product gave: C, 50·7; H, 7·3; OMe, 45·5 ($C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%). The specific rotation in water ($c = 1 \cdot 411$) was initially $[\alpha]_{5461}^{21^\circ}$ +206·3°, $[\alpha]_{5780}^{21^\circ}$ +183·5°, $[\alpha]_D^{21^\circ}$ +179·5°; falling after about 4 hours to $[\alpha]_{5461}^{20^\circ}$ +17°. The specific rotation in benzene ($c = 0 \cdot 86$) was $[\alpha]_{5461}^{21^\circ}$ +203·5°, the solution showing no mutarotation.

Polymeride of 2 : 3 : 4-*Trimethyl* l-*Arabonolactone*.—When the syrupy (unnucleated) lactone was left for some weeks in a closed vessel containing a trace of the vapour of acetyl chloride (and presumably also of hydrogen chloride), it was transformed to a solid, apparently amorphous mass. This was triturated with ether, and after filtration an insoluble, white powder was obtained. The ethereal solution, on evaporation, left a minute quantity of syrup, which was probably the unchanged lactone or an admixture of its lower polymerides. The same polymeride was obtained when the pure crystalline lactone was left during 3 days, along with a tube containing a little acetyl chloride, in a desiccator which was opened occasionally to admit moist air. In this case, the lactone was transformed to the polymeride without becoming liquid. The transformation was also produced (i) by direct treatment of the simple lactone with liquid acetyl chloride, and (ii) by leaving the crystalline lactone in an atmosphere containing hydrogen chloride gas. In the latter case, the change was accompanied by liquefaction, the product afterwards solidifying.

The solid polymeride was sparingly soluble in cold water and slightly more soluble in hot water. At 90°, this solution ($c = 0 \cdot 39$) showed no appreciable rotation in a 2-dm. tube. On cooling, a slight opalescence appeared, producing a sediment which was negligible in amount. The solution was slightly lævorotatory, very faintly acid to litmus, and did not reduce Fehling's solution. On evaporation to dryness, the polymeride was recovered quantitatively quite free from oil or other products.

The polymeride obtained by any of the methods already described could be purified from benzene–light petroleum and afterwards from benzene alone. From these solvents, the product separated in colloidal form and afterwards became micro-crystalline; m. p. 135—138°, sintering at about 130° [Found: C, 50·4; H, 7·5; OMe, 46·3; *M*, ebullioscopic in benzene, 1900 ($c = 1·05$), 2100 ($c = 2·25$). The decameric form (II), $(C_8H_{14}O_5)_{10}$, requires C, 50·5; H, 7·4; OMe, 48·9%; *M*, 1900. The open-chain formula (III), $(C_8H_{14}O_5)_{10}+H_2O$, requires C, 50·05; H, 7·4; OMe, 48·5%; *M*, 1918].

Depolymerisation.—The polymeride was quantitatively converted into the simple lactone, $C_8H_{14}O_5$, by heating in a bath at 175° under 0·03 mm. pressure. After the heating had been continued at this temperature for ½ hour, the product distilled, leaving no residue, and completely solidified spontaneously without further purification. The monomeric lactone thus regenerated had m. p. 42° and was identical with the original lactone.

When the polymeride was dissolved in a 50% excess of *N*/10-caustic soda and heated at 100° during 20 minutes, it was completely transformed to sodium trimethyl *l*-arabonate (Found: equivalent of alkali, 8·45 c.c. Calc.: 8·2 c.c.). An amount of *N*/10-hydrochloric acid exactly equivalent to the alkali present was then added, the solution evaporated to dryness at 30° in a vacuum, and the residue extracted with a little cold ether; the syrupy lactone (m. p. 45°) was thus recovered, and this solidified at once on nucleation with the original preparation of 2 : 3 : 4-trimethyl arabonolactone, with which it was shown to be identical by a determination of the mixed melting-point. When the polymeride was dissolved in the exact equivalent of *N*/10-sodium hydroxide (calculated on a simple lactone formula), and the solution heated at 100° during 20 minutes, there remained a 6% excess of alkali, showing that depolymerisation was not quite complete. The specific rotation of the polymeride in benzene ($c = 0·6$) was $[\alpha]_{5461}^{21^\circ}$ +39°, the solution not showing mutarotation.

The authors express thanks to Mr. V. S. Nicholson, B.Sc., for assistance given in this work.

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[*Received, February 17th,* 1927.]

CXIII.—*The Influence of Different Centres of Absorption on the Spectra of Substances.*

By John Edward Purvis.

The author (J., 1925, **127**, 2771; 1926, 775) has shown that the specific and general absorption of various esters is controlled by the nature and type of the basic and acidic constituents, and, in other substances, by the nature and type of the different absorbing centres in the molecule. The observations have been continued with other esters and substances possessing various centres of absorption.

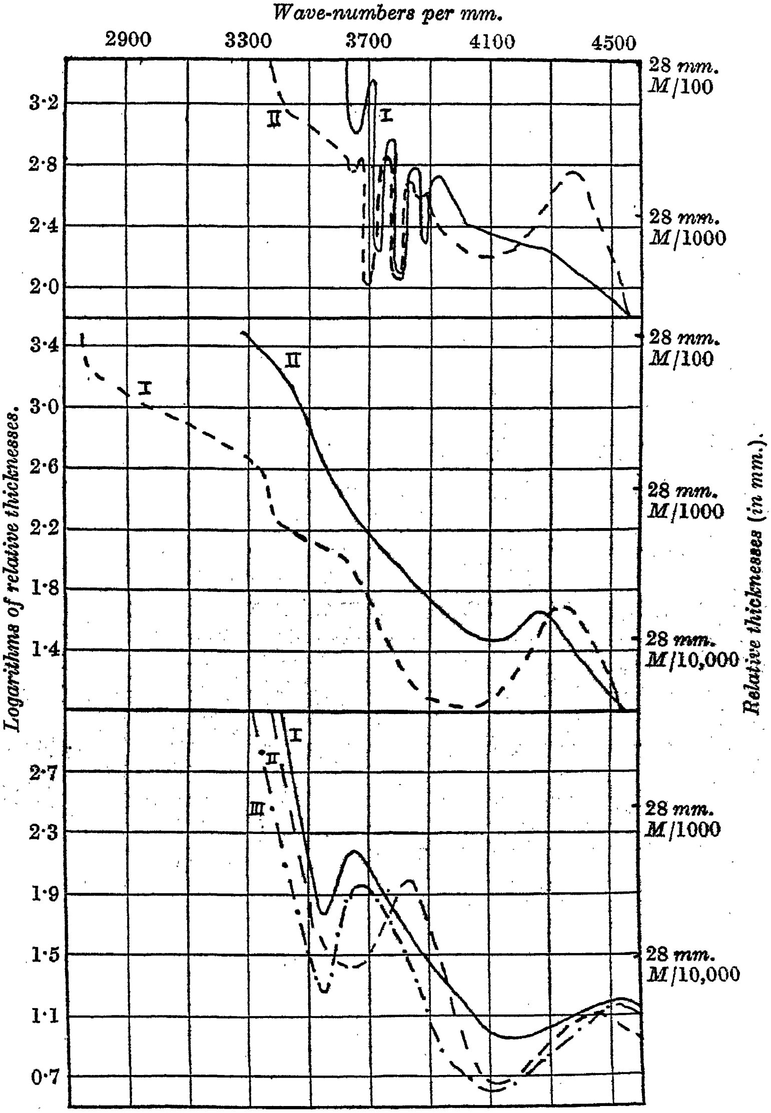
Benzyl Phenylacetate.—The curve (Fig. 1, upper curves) shows the remnants of several benzene bands which are not unlike those of toluene (J., 1915, **107**, 965); and the rapid extension of the rays between 1/λ 4030 (λ 2480) to 1/λ 4250 (λ 2352) indicates the remainder of the well-known benzene bands in this region. The author has shown (*loc. cit.*) that these remnant benzene bands occur in phenylacetonitrile, benzyl chloride, benzylidene chloride, and phenylacetic acid, the slight differences being in their position and intensities. In each of these substances the benzene residue retains a certain measure of freedom. Crymble, Stewart, Wright, and Glendinning (J., 1911, **99**, 451) state that phenyl acetate has one moderately weak band at about 1/λ 3880 (λ 2576). Acetic acid has no band.

Phenylacetaldehyde.—The curve (Fig. 1, upper curves) indicates that this substance also shows some residues of the original benzene bands. In addition, there is a weak acetaldehyde band between 1/λ 3420 (λ 2923) and 1/λ 3600 (λ 2777). Acetaldehyde itself shows a band at about 1/λ 3500 (λ 2856) as first shown by the author and McCleland (J., 1912, **101**, 1810).

Benzoin. Benzoinoxime.—In benzoin, the curve (Fig. 1, middle curves) shows a rapid absorption of the rays towards the red end and a fairly large band at about 1/λ 4000 (λ 2498), whereas in the oxime this absorption is not so well marked and the band at 1/λ 4130 (λ 2420) is considerably reduced. These results are comparable with those for benzil as described by Hantzsch and Schwiete (*Ber.*, 1916, **49**, 213), who confirmed the earlier observations of Baly and Stewart (J., 1906, **89**, 502). The benzoinoxime curve is also comparable with those of the benziloximes described by Hantzsch (*Ber.*, 1910, **43**, 1651).

Benzoic Anhydride. Benzoyl Peroxide. Phenyl Benzoate.—The curves (Fig. 1, lower curves) of these three substances, in their general form, are not unlike the curve of benzoic acid, and differ only in strength and position. The author has shown (J., 1915, **107**,

Fig. 1.

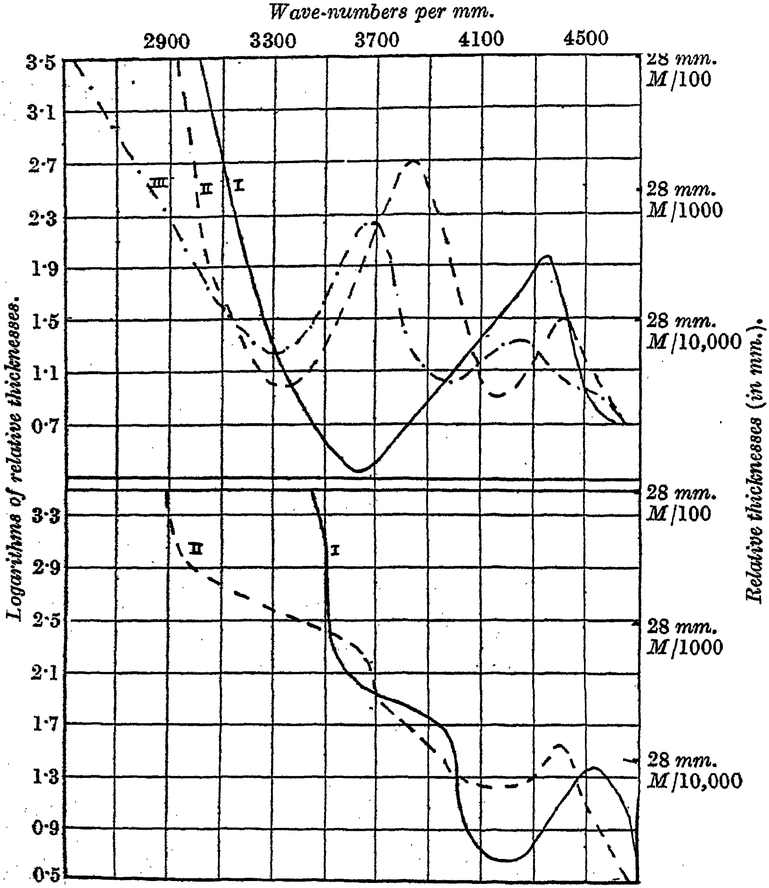


Upper curves : I *Benzyl phenylacetate* (—). II *Phenylacetaldehyde* (— —).
Middle curves : I *Benzoin* (— —). II *Benzoinoxime* (—).
Lower curves : { I *Phenyl benzoate* (—). II *Benzoyl peroxide* (— —).
III. *Benzoic anhydride* (— - —).

966) that various benzoates also differ from benzoic acid only in the strength and position of the bands.

Benzyl Salicylate. Benzyl Cinnamate.—Hartley (J., 1888, **53**, 641) first described the two bands of salicylic acid. The author (*loc. cit.*) compared salicylic acid with a number of salicylates, and noticed differences dependent on the nature and type of the base.

FIG. 2.



Upper curves: { I *Benzyl cinnamate* (—). II *Benzyl salicylate* (— —).
III *Thiosalicylic acid* (— · —).
Lower curves: I *Phenylurethane* (—). II *Phenylbenzylurethane* (— —).

The curve of benzyl salicylate (Fig. 2, upper curves) shows the two bands of salicylic acid, but there is no appearance of any of the residues of the benzene bands like those which appear in benzyl phenylacetate. Similarly, benzyl cinnamate (Fig. 2, upper curves) shows the strong band of cinnamic acid at 1/λ 3620 (λ 2760) as first described by Stewart (J., 1907, **91**, 199). In each case, the general form of the curve is similar to that of the original acid, the slight differences being in position and intensity.

Thiosalicylic Acid.—The curve (Fig. 2, upper curves) is similar to that of salicylic acid, except that the bands are shifted a little more towards the red end, and the line of general absorption is also more towards the red end. Hantzsch and Scharf (*Ber.*, 1913, **46**, 3570) noticed similar differences in a comparison of benzoic and thiobenzoic acids.

Phenylurethane. Phenylbenzylurethane.—The curve of phenylurethane (Fig. 2, lower curves) shows a large band at 1/λ 4200 (λ 2380). The phenylbenzylurethane shows a weaker band in the same region, but the line of general absorption shifts rapidly towards the less refrangible regions. None of the well-known benzene bands is visible in either substance. Urethane itself gives no absorption bands (Brannigan, Macbeth, and Stewart, J., 1913, **103**, 406) and it is very transparent.

These results, therefore, confirm the author's previous observations of other organic salts and esters in that the absorptive capacity of the basic and acidic parts is modified, and is no longer exactly the same as that of the free base or free acid. The various centres of absorption in any compound, in fact, do not act independently of each other; each centre modifies that of other centres to such an extent that one centre may overpower the influence of the others, as, for example, in the extreme cases of benzyl salicylate and benzyl cinnamate, in which the benzyl bands disappear.

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[*Received, November 29th,* 1926.]

CXIV.—*The Glow of Arsenic.*

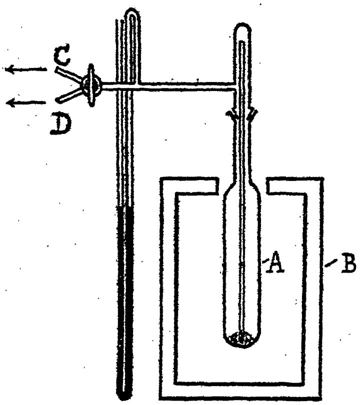
By HARRY JULIUS EMELÉUS.

THE glow of arsenic is a feebly luminous and relatively cool flame which is observed in the oxidation of this element just below the ignition point. This mode of combustion differs from normal burning in that heat must be supplied to maintain the flame, which is of such a low intensity that it can be seen only in a dark room. According to Joubert (*Compt. rend.*, 1874, **78**, 1853) the oxygen pressure has to be below a certain value for the occurrence of this phenomenon. Bloch (*ibid.*, 1909, **149**, 775) found the product of the glow to be arsenic trioxide mixed with a little pentoxide. He could detect neither ionisation nor the presence of ozone in the gas passing away from the flame. The experiments described below were made to investigate the "glow pressure" effect mentioned by Joubert (*loc. cit.*), and to compare this and other features of the oxidation of arsenic with the glow of phosphorus.

Two methods were used. In the first, the rate of pressure change in a closed system, resulting from the condensation of the arsenic trioxide formed, was observed. It was found that during the non-luminous stage of the reaction there was a slow absorption of oxygen, but that when the arsenic was glowing the rate of decrease of pressure was much greater. Secondly, visual observations were made of the temperature at which arsenic began to glow on being slowly heated in a stream of gas under various conditions.

The arsenic was freed from oxide by volatilising the latter in a vacuum at 280°. The element itself was then sublimed at 400°, and the product broken up and sieved between meshes 20—8. About 3 g. were packed round a thermometer bulb in A (Fig. 1), and the apparatus was heated to 300° by a burner, water vapour being removed by a pump attached *via* phosphorus pentoxide guard-tubes at C. Dry oxygen was admitted at D from a cylinder, and the electrically heated furnace, B (10 cm. internal diameter), adjusted to the required temperature, was raised to envelop A. The decrease of pressure per minute was recorded as soon as a contraction began; the pressure was then diminished by a few cm. of mercury, fresh readings were taken, and so on.

FIG. 1.



The general nature of the results was as follows. The formation of arsenic trioxide started well below 200°. At temperatures between 250° and 310° the rate of oxidation increased slightly as the pressure was decreased, the reaction being non-luminous. At a certain critical pressure—the "glow pressure"—the rate of oxidation suddenly increased, and a glow appeared near the arsenic surface. Simultaneously the temperature rose by about 7°.

Two experimentally-determined curves are shown in Fig. 2. These illustrate both the break in the oxidation rate and the influence of temperature on its position. From 6 to 10 such sets of observations could be made with one sample of arsenic, provided that this was heated in a vacuum between each set to remove oxide, and that water vapour was excluded. The presence of aqueous vapour permanently retarded the reaction, probably owing to the formation of non-volatile films on the arsenic grains.

The glow pressure was found to depend both on the temperature and on the length of the tube which was heated in the furnace. The curve in Fig. 3 shows a set of observations illustrating the influence of temperature (the tube was 16 cm. long and of 2·8 cm. internal diameter, 6 cm. being heated in the furnace). In form, this curve corresponds with those obtained by Scharff in studying the influence of temperature on the glow pressure of phosphorus and some of its compounds (*Z. physikal. Chem.*, 1908, **62**, 179).

FIG. 2.

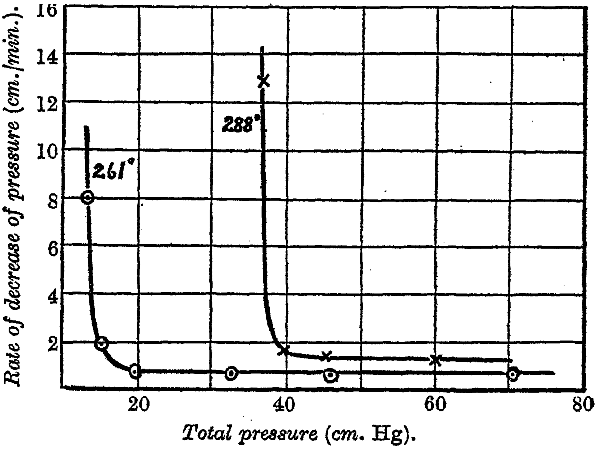
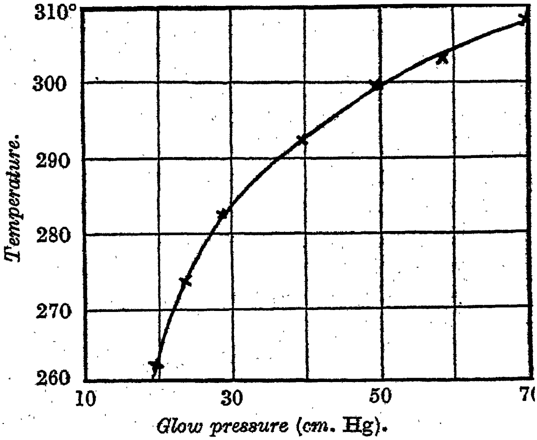


FIG. 3.



The length of tube heated was measured from the bottom to the sharply-defined zone where the oxide condensed. Table I shows the effect of varying this distance in a series of experiments. The same tube was used as before, the temperature being 292° ± 1°.

TABLE I.

Length of tube heated (cm.) ...	16	13	10·2	7·2	5·7
Glow pressure (cm. of mercury)	8	14	19	29	38

For different samples of arsenic the observed value of the glow pressure varied by less than 4 cm. This variation is probably due to the very large influence of the conditions of heating. A number of experiments made with oxygen–nitrogen mixtures showed that a glow pressure existed in this case also. The results were not readily compared with one another, however, owing to changes in the composition of the gas mixture during the non-luminous stage of the oxidation.

Experiments in Gas Streams.—The object of these was to compare the temperatures at which the glow started in air and in oxygen, and to find if certain vapours which inhibit the glow of phosphorus have any effect on that of arsenic. Apparatus similar to that shown in Fig. 1 was employed. The preheated gas stream was introduced by a side tube 1 cm. above the arsenic surface, and the temperature was raised slowly until a glow was observed. The main conclusions from these experiments were:

1. The temperature at which the glow appeared increased with the length of tube in the furnace, varying from 210° to 290°. The temperatures were lower than in stationary gas at the same pressure.
2. The glow occurred in oxygen at a temperature about 10° higher than in air under otherwise identical conditions.
3. No effect was produced on the glow temperature if the air used was saturated at room temperatures with carbon tetrachloride or nitrobenzene, or was diluted with 10% by volume of sulphur dioxide. All these substances inhibit the glow of phosphorus, though they are not among the most active. Many of the stronger poisons are thermally decomposed at the temperature at which arsenic glows.

The Cause of the Glow Pressure.—The foregoing experiments show that the glow of arsenic does not occur until the pressure is reduced. The cause of this is indicated in Table I, where it is shown that the greater the distance from the arsenic surface to the zone where the oxide condenses the less readily the glow occurs. From this it appears that the oxide itself hinders the reaction, this effect becoming smaller the steeper the concentration gradient which determines its removal by diffusion. This may be due to retardation of the reaction owing to the accumulation of its product, or, alternatively, it may be ascribed to a specific inhibitory action, similar to the inhibition of the glow of phosphorus by substances such as ethylene.

The effect of reduction of pressure in promoting the glow may similarly be due to an acceleration of the removal of oxide. It is known that a substance evaporates at a greater rate at low pressures than at high, the relation between the rate of evaporation v, the total pressure P, and the partial pressure of the evaporating substance p', being $v = c \log P/(P - p')$, where c is a constant (Stefan, *Sitzungsber. Akad. Wiss. Wien*, 1873, **68**, 385; compare also Ewan, *Phil. Mag.*, 1894, **38**, 505). The conditions in the present case are similar to those considered by Stefan. Evaluating this expression for the vapour pressure at, *e.g.*, 291°, the relative rate of evaporation is found to increase rapidly below a certain total pressure, as shown in Table II ($p' = 6{\cdot}54$ cms.).

TABLE II.

Total pressure, P (cm. Hg) ...	60	40	20	15	10	8	7
$\text{Log}_{10} P/(P - p')$	0·05	0·08	0·17	0·25	0·46	0·74	1·18

The pressure at which a rapid rate of evaporation sets in depends on the partial pressure of the oxide, and therefore on the temperature. Its variation with temperature is, moreover, similar to that of the glow pressure itself. If the above conception is correct, the production of the glow of arsenic on reducing the pressure may be considered as due, at least in part, to an acceleration of the removal of oxide, and hence of the reaction itself.

Analogy with the Glow of Phosphorus.—The chemical similarity of arsenic and phosphorus extends to their phosphorescent flames. In neither case does the luminous oxidation in oxygen start until the pressure is reduced. In each instance, the higher the temperature the less is the requisite pressure reduction. The non-luminous reaction preceding the glow is, however, much more vigorous for arsenic than for phosphorus (Rayleigh, *Proc. Roy. Soc.*, 1924, *A*, **106**, 1), and the experiments indicated that the ease of removal of the oxide so formed largely determined the occurrence of the glow. No corresponding phenomenon is known in the oxidation of phosphorus.

The glow of phosphorus occurs at considerably higher temperatures in oxygen than in air. In the case of arsenic, these two temperatures were found to be more nearly the same, and the difference could be ascribed to a larger formation of oxide in oxygen. Three substances which inhibit the glow of phosphorus are without influence on that of arsenic. It is possible, however, that others will be found capable of inhibiting the latter reaction also.

The author wishes to express his gratitude to Professor H. B. Baker, in whose laboratory these experiments were carried out, for his interest and advice. The research has been conducted during the tenure of an 1851 Senior Studentship.

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[*Received, January 18th,* 1927.]

CXV.—*The Origin of the Ultra-violet Spectrum of the Glow of Phosphorus.*

By HARRY JULIUS EMELÉUS and RONALD HERBERT PURCELL.

THE spectrum of the light from glowing phosphorus is continuous in the visible region and shows five groups of bands in the ultra-violet at about λ 3419—3245, 2633—2594, 2552—2527, 2477—2451, 2393—2371 Å.U. (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235; Petrikaln, *Z. Physik*, 1924, **22**, 119). They have been observed in the normal flame of phosphorus (Emeléus and Downey, J., 1924, **125**, 2491), in the glow of phosphorus trioxide, and in the flame of phosphine (Emeléus, J., 1925, **127**, 1362). The band at λ 3270 was recorded by Hartley (*Phil. Trans.*, 1894, **185**, 168), who introduced phosphorus pentoxide into the oxy-hydrogen flame. These bands were also measured by Geuther in a comprehensive survey of the phosphorus spectra (*Z. wiss. Phot.*, 1907, 5, 33); he obtained them, together with other bands apparently not present in the glow, on volatilising potassium phosphate in the carbon arc. Other ways of producing what is apparently the same spectrum are described in Kayser's Handbuch (Vol. VI), but from none of these methods can the origin of the bands be determined unambiguously.

The experiments described below consist in an examination of the ultra-violet spectrum of the phosphorescence of phosphorus pentoxide, and of the discharge through its vapour. Ebert and Hoffmann (*Z. physikal. Chem.*, 1900, **34**, 80) found that phosphorus pentoxide exhibited a strong phosphorescence after illumination, especially at low temperatures. They recorded the visible spectrum as continuous, with a maximum intensity in the green, a result which was confirmed in the present work during an unsuccessful search for ultra-violet bands. The discharge through phosphorus pentoxide vapour gave a complex band system, in which were included the bands of the spectrum of glowing phosphorus. Finally, a re-examination of the latter phenomenon was made, revealing other bands common to these two spectra.

The Spectrum of the Phosphorescence of Phosphorus Pentoxide.—The spectrographs used were a Hilger quartz instrument (size E6), for the loan of which the authors are indebted to the Air Ministry, and a large-aperture quartz spectrograph of special construction. This had two lenses working at an aperture of *f* 4·5 and a Cornu prism of 7·5 cm. base. The dispersion at λ 2550 was approximately 30 Å.U. per mm.

The apparatus used in photographing the spectrum of the phosphorescence at liquid-air temperatures is shown in Fig. 1. Pure phosphorus pentoxide was distilled in a vacuum on to the outer surface of the inner tube, T, from a tube having a ground glass joint interchangeable with J. The outer tube (shown in position), with a quartz window, W, attached by wax, was then quickly replaced and the interspace was kept exhausted by a diffusion pump. Liquid air was poured into the inner tube, T, as required.

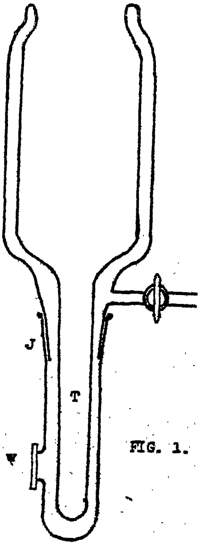


FIG. 1.

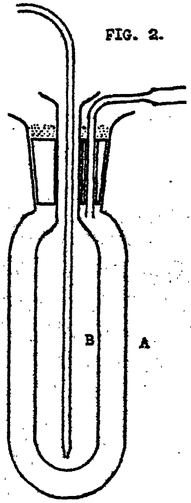


FIG. 2.

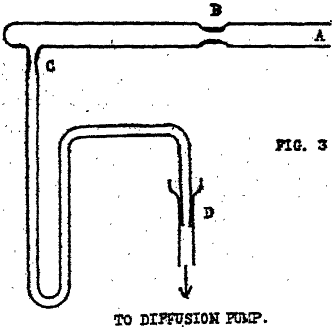


FIG. 3

In Fig. 2 is shown a simpler device used for studying the phosphorescence of phosphorus pentoxide cooled to about − 50° by carbon dioxide. The outer tube, A, was of clear quartz, and phosphorus pentoxide was sublimed directly from it on to the inner tube. Cooling was effected by carbon dioxide, which was delivered from a cylinder and passed through a fine jet at the end of a copper tube inserted into the inner vessel.

The relatively feeble phosphorescence at the ordinary temperature was photographed by filling a silica tube with the pentoxide.

Blank experiments were made to examine the phosphorescence of the silica tube itself.

The pentoxide was illuminated in each case by a condensed spark between aluminium poles placed 1 cm. from the apparatus containing the oxide. A jet of water playing on the silica opposite the spark kept the surface clean. A sector, synchronised with the spark, rotated between it and the slit of the spectrograph, placed in alinement. The pentoxide was illuminated by the spark during one-quarter of each revolution of the sector, the speed of which was varied according to the duration of the phosphorescence (which was determined by the temperature). The actual exposure of the phosphorescence was about two-thirds of the period of each revolution.

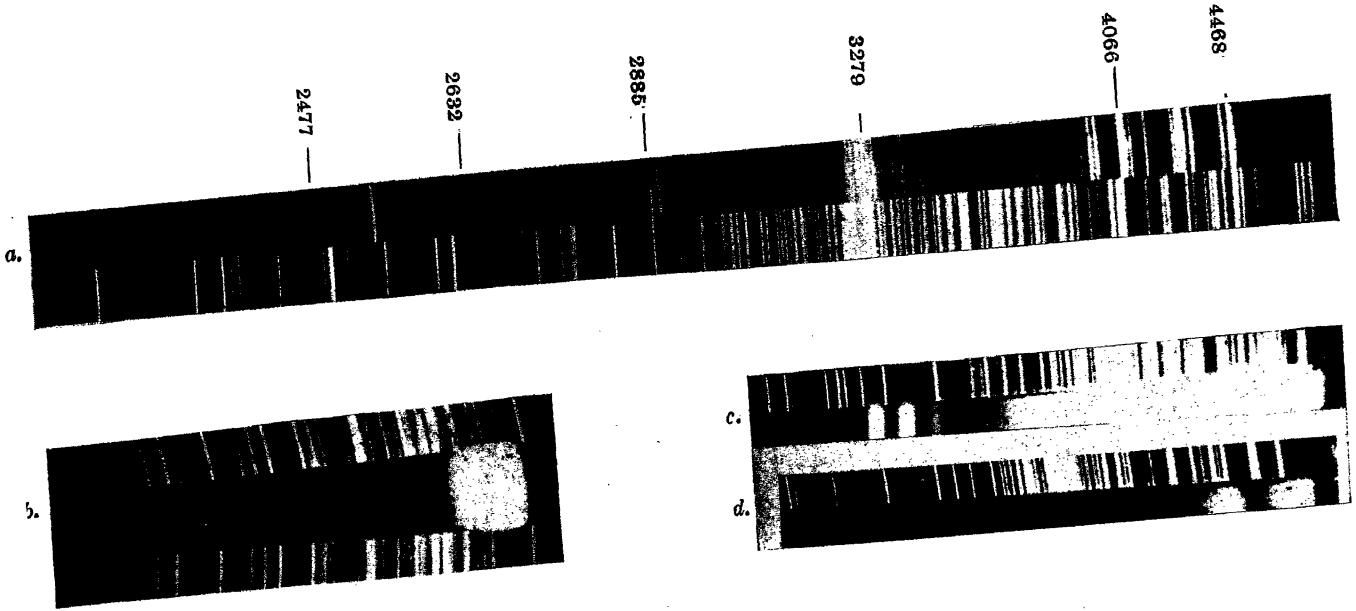
Exposures of 10—140 hours were made under the various conditions specified; in each case the band in the visible region with a maximum intensity at about λ 4600 was observed, using Ilford Monarch plates (compare Ebert and Hoffmann, *loc. cit.*). There was no evidence of an ultra-violet spectrum. A photograph showing this band is given in Plate 1 (*b*). It corresponds roughly with a broad band in the spectrum of the visible light from glowing phosphorus [Plate 1 (*d*)]. This suggests that the latter is due to the phosphorescence of phosphorus pentoxide under the action of the ultra-violet radiation emitted in the reaction.

Spectrum of the Discharge through the Vapour of Phosphorus Pentoxide.—The phosphorus pentoxide was contained in a silica tube (18 cm. long, 0·8 cm. internal diameter) with a clear end, the method of filling being as follows. The silica apparatus ACD was cleaned, dried, and connected to a diffusion pump by a mercury-sealed ground joint, D. A quantity of pure phosphorus pentoxide was introduced into BA, which was then sealed at A in the oxy-hydrogen flame. The apparatus was exhausted, with the U-tube cooled in liquid air, BC was baked out, and AB warmed. The pentoxide was distilled into BC, and AB was sealed off at the constriction B. After distilling the pentoxide four times from one end of BC to the other with the pump working, in which process much of it was transferred to the U-tube, the constriction C was sealed.

External electrodes of copper foil, with a condenser and spark-gap in the circuit, were used in exciting a discharge through the tube, which was heated electrically to 200°. The discharge was dim, and of a greenish-white colour. Exposures of up to 40 hours were needed on the Hilger spectrograph.

A complex band spectrum was observed, which was compared directly with a spectrogram of the glow of phosphorus taken on the

PLATE 1.



(a) *Spectrum of discharge through phosphorus pentoxide vapour* (2 *hours*).
(b) *Spectrum of phosphorescence of phosphorus pentoxide at* —55° (45 *hours*).
(c) *Spectrum of glow of phosphorus* (480 *hours*).
(d) *Spectrum of glow of phosphorus on panchromatic plate* (250 *hours*).
Copper-arc reference spectra.

same instrument. There was no doubt that the bands in the glow spectrum were present in the discharge, although in the latter there were many additional bands, and the isolated groups were connected by bands of low intensity. Most were narrow and degraded towards the red. The positions of the violet edges, which were fairly sharp, were measured. In certain cases, where there was no definite head, the approximate position of the violet edge of the band was again ascertained. Plate 1 (*a*) is an enlargement of this spectrum, showing the groups of narrow bands below λ 3000, and also the complex band at λ 3300—3200. Only the more intense band heads above λ 3000 are recorded, the dispersion of the instrument being small. The two narrow bands at λ 2896 and 2885 are attributed to carbon.

Table of Wave-Lengths of Violet Edges of Bands.

λ.	λ.	λ.	λ.	λ.	λ.	λ.
4468 (7)	3493 (4)	3211 (3)	2896 (7)	2689 (2)	2534 (7)	2425 (4)
4346 (9)	3469 (6)	3135 (6)	2885 (8)	2665 (4)	2533 (4)	2421 (2)
4276 (6)	3313 (4)	3129 (3)	2861 (3)	2646 (4)	2526 (2)	2405 (1)
4119 (7)	3303 (4)	3124 (3)	2840 (4)	2632 (4)	2511 (2)	2392 (2)
4066 (10)	3287 (3)	3064 (3)	2823 (4)	2617 (2)	2499 (4)	2380 (3)
3944 (7)	3279 (4)	3045 (4)	2806 (3)	2602 (4)	2488 (4)	2376 (2)
3911 (7)	3270 (6)	3008 (4)	2778 (4)	2593 (5)	2477 (5)	2368 (1)
3747 (6)	3266 (6)	2937 (3)	2762 (4)	2580 (5)	2464 (4)	2353 (2)
3726 (5)	3256 (6)	2921 (3)	2720 (1)	2553 (5)	2445 (6)	2343 (2)
3517 (4)	3246 (6)	2912 (3)	2705 (5)	2546 (4)	2432 (6)	2318 (2)

The error in the measurements below λ 3000 is probably less than 2 Å.U. The bands between λ 2200—2800 and the complex band at λ 3100—3400 appear to correspond in part with the more precise measurements of Geuther, de Watteville, and de Gramont (Kayser, *op. cit.*, p. 253), but the spectra are not identical. This can be ascribed to the low dispersion of the instrument, and the different means of excitation used in the present research. The description of this spectrum does not come within the scope of this paper. It is intended to attempt to correlate it with the absorption spectra of the oxides of phosphorus.

From these results it was concluded that the band spectrum observed in the discharge through phosphorus pentoxide was emitted from the molecule of an oxide, and that the spectrum of the glow of phosphorus had the same origin.

Re-examination of the Spectrum of the Glow of Phosphorus.—The bands described by Geuther (*loc. cit.*) include groups of low intensity at λ 2789—2647, and a group at λ 2320—2280. These and other bands observed in the discharge through phosphorus pentoxide had not been observed in the spectrum of the glow of phosphorus. The large-aperture quartz spectrograph was therefore used in a re-examination of this phenomenon. The light source was a phosphorus slab cast in a tray (Centnerszwer and Petrikaln, *loc. cit.*).

With an exposure of 480 hours the five groups of bands already known were observed. Some of the negatives showed the components of each group. The continuous spectrum extended to λ 2700, partly obscuring the band at λ 3270. Three new broad bands were also visible, although the component narrow bands of each of these groups could not be distinguished. Their approximate positions were λ 2300—2325; 2660—2700; 2740—2795. Of these new groups, only one (that at λ 2660—2700) has been satisfactorily reproduced in Plate 1 (*c*). They correspond with groups of bands recorded by Geuther, which are also present in the spectrum of the discharge through phosphorus pentoxide vapour, a fact which supports the view put forward as to the origin of the spectrum of the glow of phosphorus. A further exposure of 250 hours on a panchromatic plate showed that the spectrum of the glow of phosphorus extended into the red. What are apparently two broad bands occur at λ 5200—5900, and λ 6000—6800. The dispersion of the instrument is too small to determine if these are due to the merging of narrower bands.

Summary.

Attempts have been made to determine the origin of the spectrum of the glow of phosphorus by unambiguous means. The ultraviolet spectrum of the phosphorescence of phosphorus pentoxide was first photographed, and exhibited none of the bands occurring in the spectrum of the glow of phosphorus. The discharge through the vapour of phosphorus pentoxide in a silica tube gave a complex band spectrum, which included all the bands known in the spectrum of the glow of phosphorus. A re-examination of the latter phenomenon showed further bands common to these two spectra. It was concluded that the ultra-violet spectrum of the glow of phosphorus had its origin in the molecule of an oxide.

We wish to thank Professor H. B. Baker, F.R.S., in whose laboratory these experiments were carried out, for his keen interest and advice. We are greatly indebted to Professor A. Fowler, F.R.S., who has placed facilities at our disposal and advised us in the interpretation of the spectra. We also wish to thank Dr. W. E. Downey, who developed the apparatus and technique used in studying the phosphorescence of phosphorus pentoxide at liquid-air temperatures, for kindly giving us the benefit of his experience. One of us (R. H. P.) is in receipt of a maintenance grant from the Department of Scientific and Industrial Research; the other holds an 1851 Senior Studentship. Apparatus has been purchased from grants both from the Dixon Fund of the London University and from Messrs. Brunner Mond and Co., Ltd.

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CXVI.—*The Burning of Carbon Disulphide near the Limit for the Propagation of Flame, with some Remarks on the Ignition Point of Sulphur.*

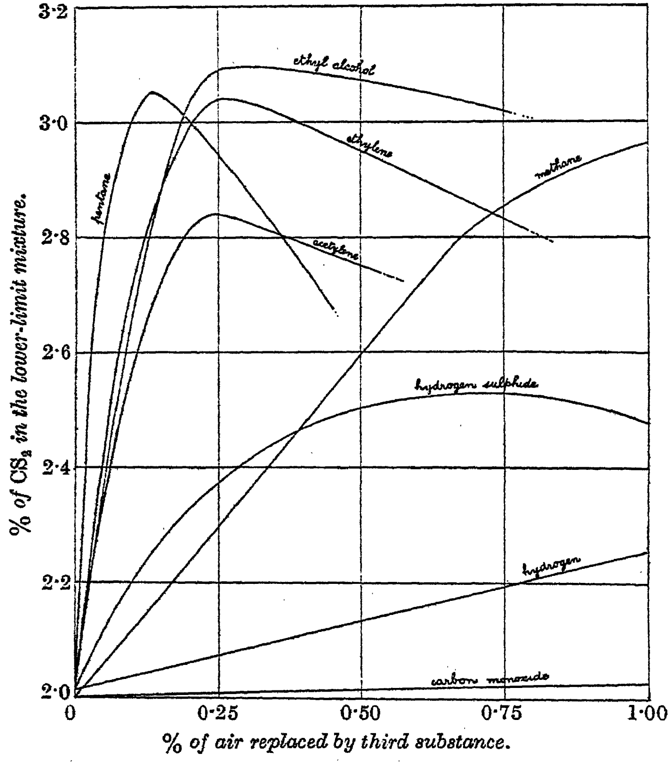
By ALBERT GREVILLE WHITE.

IN a communication on limits for the propagation of flame in mixtures containing air and more than one vapour (J., 1922, **121**, 2561), it was shown that the addition of small quantities of the vapour of ethyl ether, benzene, acetone, or acetaldehyde to carbon disulphide–air caused a pronounced contraction of the propagation range. This was most noticeable at the lower limit, where very small quantities of added vapour *increased* considerably the amount of disulphide present at the limit, although the addition of larger quantities of the vapours reduced the amount of disulphide necessary to give a limit mixture. It was thus found possible to divide the propagation range into two parts, giving four limits instead of the normal two. A similar division for ethyl ether–air is described in the same communication, but this phenomenon relates to the upper limit, near which ether–air mixtures can often propagate a cool flame. It was presumed that propagation at the limit in carbon disulphide–air was catalysed by some product of the combustion, but that this catalysis was inhibited by certain vapours, although not appreciably affected by similar quantities of carbon monoxide, dioxide, or tetrachloride, or of hydrogen.

Phenomena apparently connected with the above were reported on the ignition point of carbon disulphide mixtures by Frankland (*Chem. News*, 1862, **6**, 3), whose work has recently been extended by Dixon (*Rec. trav. chim.*, 1925, **44**, 305), and by Delépine (*Bull. Soc. chim.*, 1922, **31**, 762) for the spontaneous oxidation of certain sulphur compounds in air. Dixon suggests that carbon monosulphide catalyses the phosphorescent combustion of the disulphide, and that the inhibitors act by condensing on the surface of the monosulphide. Delépine found that certain compounds in which sulphur was doubly bound to carbon or phosphorus oxidised in air at the ordinary temperature. This oxidation was apparently stopped by the products of the reaction, and was markedly hindered by traces of ethyl ether or acetaldehyde, and to some extent by ethyl alcohol and benzene. It was promoted by fixed alkali or ammonia, and also by the lower saturated aliphatic acids. He favoured an explanation similar to that advanced by Moureu and Dufraisse to account for the behaviour of "antioxygens" in autoxidation (J., 1925, **127**, 1), in which the compound first produced is assumed to be a peroxide.

Fig. 1.

Showing the value of the lower limit for carbon disulphide–air when part of the air is replaced by a third substance.



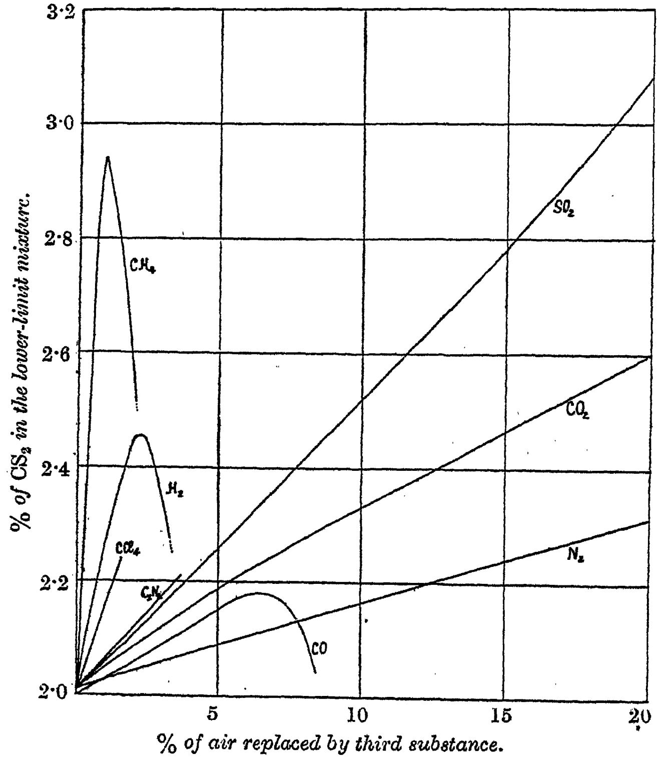
The present work consists largely of an extension of the former results. All limits were determined for downward propagation at the ordinary temperature and pressure in glass tubes 5 cm. in diameter and 150 cm. long. The preparation and ignition of the mixtures were carried out as previously described (J., 1922, **121**, 1244, 2561; 1924, **125**, 2387). Tables I and II show the limits for the propagation of flame in mixtures of various gases and vapours with carbon disulphide and air. All are lower limits except in the one case specified. Compositions are given in percentages by volume.

The calculated limits are those given by Le Chatelier's rule, assuming the values 4·0% and 12·0% for the carbon disulphide limits. The results are shown graphically in Figs. 1 and 2.

The two combustibles present sometimes appeared to burn separately, as two flames were obtained touching only near the axis of the tube. This was well marked for a mixture of carbon monoxide, carbon disulphide, and air containing 7·9% of the monoxide.

FIG. 2.

Showing the value of the lower limit for carbon disulphide–air when part of the air is replaced by a third substance.



The present results are in general agreement with former work, and indicate that the addition of a small quantity of a large variety of substances raises the value of the lower limit for carbon disulphide–air. The large difference formerly noted between the behaviour of gases and that of certain vapours is now seen to have been due in part to the choice of gases, and in part to the small quantities of these that were used. The added substances appear

TABLE I.

Original temperature of mixtures, 15° ± 3°.

Combustible mixture.			Limit (calc.).	Error %.
H_2.	CS_2.	Both.		
—	2·01	2·01		
0·30	2·08	2·38		
0·70	2·18	2·88		
1·31	2·32	3·63		
1·90	2·43	4·33		
2·44	2·45	4·89	5·54	+13
4·10	2·05	6·15	6·35	+ 3
5·15	1·71	6·86	6·86	0
5·81	1·45	7·26	7·20	− 1
7·49	0·74	8·23	8·09	− 2
9·0	—	9·0		
CO.	CS_2.	Both.		
—	2·00	2·00		
0·95	2·02	2·97		
2·00	2·05	4·05		
4·00	2·11	6·11		
5·60	2·17	7·77	8·6	+11
7·90	2·12	10·0	9·7	− 3
9·1	1·80	10·9	10·6	− 3
10·4	1·33	11·7	11·8	+ 1
11·8	1·00	12·8	12·8	0
13·8	0·50	14·3	14·2	− 1
15·7	—	15·7		
C_2H_4.	CS_2.	Both.		
—	2·01	2·01		
0·04	2·36	2·40		
0·07	2·58	2·65		
0·16	2·92	3·08		
0·25	3·04	3·29		
0·32	3·00	3·32		
0·43	2·99	3·42	3·92	+15
0·96	2·70	3·66	3·83	+ 4
1·54	2·16	3·70	3·74	+ 1
2·23	1·38	3·61	3·62	0
2·72	0·80	3·52	3·54	+ 1
3·42	—	3·42		
EtOH.	CS_2.	Both.		
—	2·01	2·01		
0·06	2·42	2·48		
0·09	2·63	2·72		
0·10	2·65	2·75		
0·14	2·87	3·01		
0·25	3·09	3·34		
0·33	3·08	3·41		
0·46	3·08	3·54	3·99	+13
0·87	2·91	3·78	3·98	+ 5
1·58	2·36	3·94	3·96	+ 1
2·38	1·59	3·97	3·94	− 1
3·90	—	3·90		

Combustible mixture.			Limit (calc.).	Error %.
H_2.	CS_2.	Both.		
(Upper limit.)				
—	34·0	34·0		
3·18	28·6	31·8		
8·3	24·9	33·2		
18·8	18·8	37·6	20·7	−45
33·8	11·2	45·0	32·3	−28
46·4	5·1	51·5	48·8	− 5
74·0	—	74·0		
CH_4.	CS_2.	Both.		
—	2·00	2·00		
0·31	2·43	2·74		
0·65	2·77	3·42		
0·80	2·88	3·68		
0·94	2·94	3·88		
1·21	2·88	4·09	4·45	+ 9
1·58	2·75	4·33	4·58	+ 6
2·40	2·40	4·80	4·84	+ 1
3·08	2·02	5·10	5·05	− 1
4·75	1·02	5·77	5·59	− 3
6·12	—	6·12		
C_2H_2.	CS_2.	Both.		
—	2·01	2·01		
0·08	2·50	2·58		
0·23	2·84	3·07		
0·29	2·83	3·12		
0·42	2·78	3·20		
0·53	2·74	3·27	3·74	+14
1·26	2·02	3·28	3·44	+ 5
1·60	1·60	3·20	3·29	+ 3
2·23	0·74	2·97	3·03	+ 2
2·80	—	2·80		
H_2S.	CS_2.	Both.		
—	2·00	2·00		
0·11	2·22	2·33		
0·28	2·40	2·68		
0·56	2·51	3·07		
0·84	2·52	3·36	4·37	+30
1·22	2·43	3·65	4·51	+24
2·07	2·08	4·15	4·82	+16
2·69	1·79	4·48	5·02	+12
4·27	1·00	5·27	5·51	+ 5
6·05	—	6·05		
n-C_5H_{12}.	CS_2.	Both.		
—	2·01	2·01		
0·013	2·31	2·32		
0·05	2·81	2·86		
0·08	2·95	3·03		
0·13	3·05	3·18		
0·23	2·96	3·19	3·57	+13
0·46	2·67	3·13	3·20	+ 2
0·71	2·18	2·89	2·83	− 2
1·08	1·15	2·23	2·20	− 1
1·34	0·44	1·78	1·77	− 1
1·49	—	1·49		

TABLE II.

Original temperature of mixtures, 16° ± 3°.

$_2$.	CS_2.	CO_2.	CS_2.	SO_2.	CS_2.	C_2N_2.	CS_2.	CCl_4.	CS_2.
—	2·01	—	2·01	—	2·01	—	2·01	—	2·01
3·8	2·07	4·0	2·15	1·8	2·09	1·9	2·11	0·75	2·12
7·6	2·13	6·0	2·22	5·5	2·28	3·0	2·16	1·6	2·24
14·2	2·23	8·0	2·28	10·0	2·52	3·7	2·21		
23·3	2·35	12·0	2·38	15·0	2·78				
40·9	2·63	20·0	2·60	20·0	3·08				

to function in three ways: (1) They alter the thermal constants of the mixture; (2) they alter the percentage of oxygen in the mixture; (3) they produce what may be termed a specific catalytic effect.

(1) The alteration of thermal constants would affect any mixture of air with a combustible, and is chiefly responsible for such phenomena as the greater extinguishing effect of carbon dioxide as compared with nitrogen.

(2) A small change in the oxygen content of a mixture usually causes only a small change in the lower limit except when the combustible : oxygen ratio is large, as when ammonia burns in air, or when much inert gas is used with a normal combustible. In the case of carbon disulphide (and, to a less extent, of hydrogen sulphide), however, this effect persists even when a large proportion of oxygen is present, as is seen from Table III. The difference between these substances and methane is illustrated in Fig. 3.

TABLE III.

Original temperature of mixture, 16° ± 3°.

% O_2 in mixture.	% CS_2 in lower-limit mixture.	% O_2 in mixture.	% H_2S in lower-limit mixture.
11·8	2·63	15·6	6·60
15·5	2·35	17·6	6·25
17·4	2·23	19·7	6·05
19·7	2·07	28·0	5·56
20·6	2·00	35·4	5·30
37·0	1·59	51·0	5·04
53·2	1·40	66·6	4·93
93·0	1·24		

Table IV shows that ether–carbon disulphide mixtures are similarly affected when 19·7% of oxygen is added. Here the magnitude

TABLE IV.

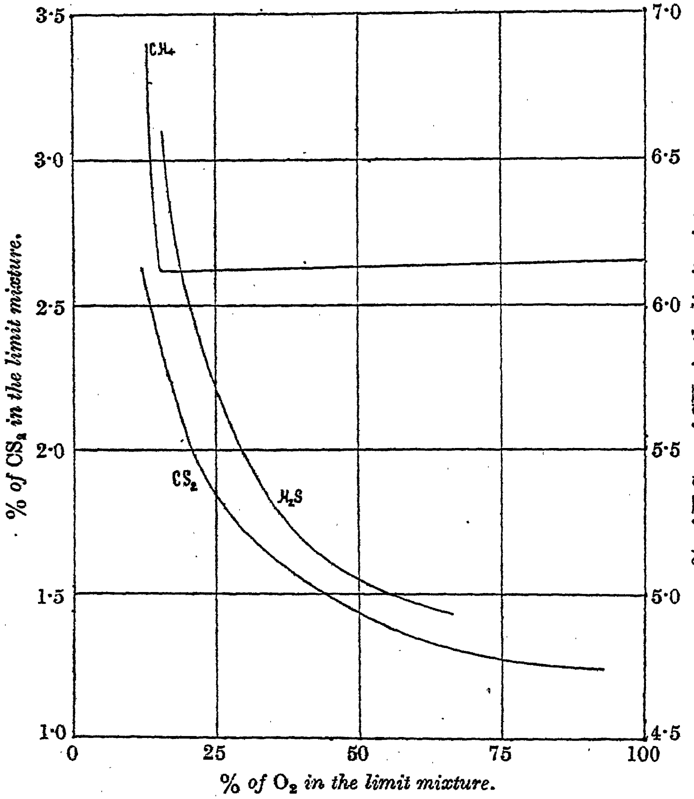
Original temperature of mixture, 15° ± 2°.

% CS_2 in combustible	100	98·5	95·0	85·0	75·0	50·0
% Ether in combustible	—	1·5	5·0	15·0	25·0	50·0
Limit in air	2·00	2·79	3·23	3·30	3·10	2·58
Limit when mixture contained 19·7% of added oxygen	1·61	2·36	2·88	2·98	2·84	2·42

of the effect decreases with decreasing proportion of disulphide, but it is still noticeable when the amount of ether is sufficient to inhibit the specific catalytic effect observed when small quantities of combustible vapours are added to carbon disulphide–air mixtures. This agrees with the fact that the addition of small quantities of several combustible substances to hydrogen sulphide–air was found to reduce the amount of hydrogen sulphide needed to give a limit mixture. This effect of oxygen content on the lower limit appears to be a property conferred by sulphur on certain of its compounds, but does not appear to be intimately connected with the catalytic effect originally observed.

FIG. 3.

Showing the effect of varying oxygen content on the value of the lower limit for carbon disulphide, hydrogen sulphide, and methane.



Except when oxygen is added, any change in the oxygen content of a mixture depends only on the volume of the material added, so that, volume for volume, all substances should produce equal effects from this cause. An upper limit to its value can be obtained from the results given by the addition of nitrogen, since the thermal constants of the mixture are hardly affected thereby. This effect is relatively small, and for most combustibles the rise in the lower limit is far greater than could be attributed to it, even when coupled with any change in the thermal constants of the mixture.

(3) The catalytic effect is the most important and varies tremendously from one substance to another. A comparison of the nitrogen figures with those for carbon monoxide and for cyanogen indicates that in both these cases the residual effect must be small, but for such substances as pentane and ethylene it is overwhelmingly great. This specific catalytic effect seems to be most pronounced for combustibles, although the difference found between carbon dioxide and sulphur dioxide indicates that the effect of the latter substance is greater than would be expected if due to its thermal properties alone. Carbon monoxide and cyanogen, which contain no hydrogen, behave almost as incombustibles; but the effect does not appear to be proportional to the amount of hydrogen in a compound, as may be seen by comparing the amounts of various substances needed to produce the same effect when small quantities are used. The order of efficacy of certain of those tested appears to be : Pentane and ethyl ether, acetaldehyde, ethylene, ethyl alcohol, acetylene, benzene, acetone, hydrogen sulphide, acetic acid, methane, hydrogen, cyanogen, carbon monoxide. This order suggests that ease of oxidation might prove to be an important factor. The relative positions of hydrogen and hydrogen sulphide also seem to point to the molecular nature of the effect, but the high thermal conductivity of hydrogen may be partly responsible for the small effect produced by this gas. Experiments with acetone and hydrogen showed that when used together they produced the effect to be expected from their behaviour when used separately.

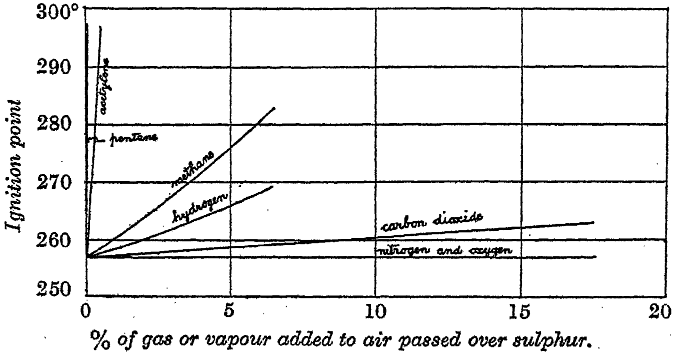
Table I shows that as small quantities of the air in a carbon disulphide–air mixture are progressively replaced by a second combustible, the increase in the amount of the disulphide needed to give a lower-limit mixture becomes smaller, until the amount of disulphide present ultimately reaches a maximum and then diminishes. The maximum is attained more quickly the greater the original effect of the second combustible. The calorific value of the limit mixture containing most carbon disulphide is generally 900—950 Cals., but for hydrogen, hydrogen sulphide, and acetylene the value found is considerably below this. These gases give lower-limit calorific values well below the normal 1100—1200 Cals. when used with air alone, so that the fall in the amount of carbon disulphide in the mixture probably sets in when the second combustible present begins to burn normally. After the amount of disulphide present has begun to diminish, the amounts of the two combustibles can be calculated approximately from Le Chatelier's rule, provided the value of the carbon disulphide lower limit be taken as 4·0%, and agreement with the rule generally becomes closer as the amount of disulphide diminishes. There is a similar tendency shown at the upper limit, but here it is not so well defined. At the lower limit, Le Chatelier's rule is followed fairly well over two-thirds or more of the range of mixtures, as measured by the amount of the second combustible present. In the presence of a minimum quantity of some other combustible, carbon disulphide behaves as though its calorific value at the lower limit was 1060 Cals., a value not very different from that normally found for vapours (J., 1922, **121**, 1244). It is important that this occurs even with carbon monoxide, which has such a very small effect in raising the value of the lower limit of the disulphide. When burning alone, carbon disulphide–air can propagate flame if the calorific value of the mixture exceeds 530 Cals. Carbon disulphide thus appears to possess two different modes of combustion, and there is no reason to doubt the explanation formerly advanced to explain the results then available, *viz.*, that the ordinary limit combustion of carbon disulphide is catalysed, probably by some product of its combustion, and that this catalysis is hindered by a large variety of substances. Of the gases known to be produced when the disulphide burns, the only one found to reduce the value of the limit was carbon oxysulphide, and this had an effect considerably less than that produced by an equal volume of the disulphide. The oxysulphide and oxygen were the only two substances tested which did not hinder the burning of carbon disulphide.

Dixon (*loc. cit.*) suggests that the product catalysing the ignition of carbon disulphide is the monosulphide of carbon. If this is the explanation of the limit results given by carbon disulphide, the phenomenon should be confined to substances containing both sulphur and carbon, such as the disulphide and oxysulphide of carbon. This idea is supported by the behaviour of hydrogen sulphide, which does not exhibit this phenomenon, whilst its lower limit is also calculable from the lower limit for hydrogen and the theoretical (calorific value) limit for sulphur. This might, however, be due to the large amount of hydrogen in the molecule.

To test the monosulphide theory it was decided to examine the effect of certain combustible substances on the ignition point of sulphur itself. To this end sulphur was heated in a glass tube 1·5 cm. in diameter. The temperature of the sulphur was taken by means of a thermometer immersed in it, whilst the necessary air for combustion was introduced by means of a side tube at the surface of the sulphur. The procedure adopted was to introduce a slow stream of air (or air containing the substance under test) through the side tube, after which the stream of gas was gradually cut off. Ignition then took place if the sulphur was just above its ignition point. For comparison, relative values of the ignition temperature of mixtures of 3% carbon disulphide–air with a third substance were determined by evacuating glass bulbs of 12—15 c.c. capacity, and then allowing the appropriate mixture to flow into the bulb. As the figures obtained have no absolute significance, the results are only shown graphically (Figs. 4 and 5), but small quantities of hydrogen sulphide also raised the ignition point of sulphur materially. There is a striking similarity between the general form of the two series of results, despite the greater magnitude of the rise produced in the case of carbon disulphide. The ignition of sulphur is materially hindered by small quantities of various substances, and is thus probably itself a catalysed phenomenon. The ignition and combustion of carbon disulphide may be catalysed by carbon monosulphide, but the occurrence of a somewhat similar phenomenon in the case of sulphur renders it extremely unlikely that the monosulphide is the sole catalysing agent.

FIG. 4.

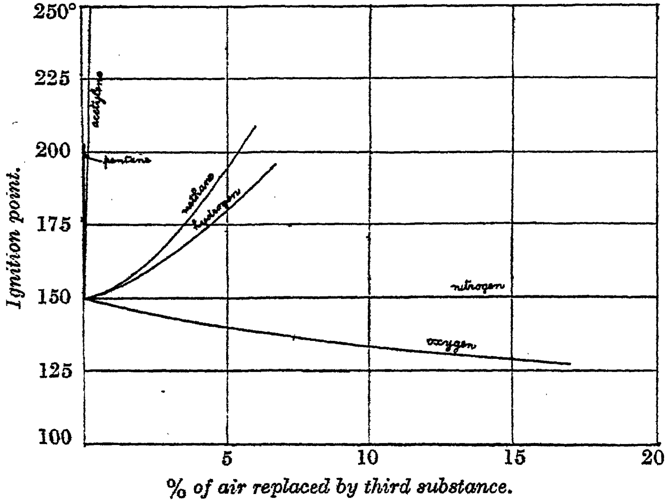
Showing the ignition point of sulphur when the air passed over it contains various substances.



Attention must be directed to certain differences between the results given by the present work and those found by Dixon. The order of efficacy of certain substances as gauged by their power of preventing the propagation of flame at the limit in carbon disulphide–air is given on p. 799. As regards their effect on the ignition of carbon disulphide, Dixon classes ethylene and acetylene as poisonous and pentane, carbon monoxide, methane, and ethyl ether as noxious, whilst hydrogen is grouped with carbon dioxide and nitrogen as inert. Delépine's work (*loc. cit.*) is probably not so closely connected with the present communication, but it is noteworthy that acetic acid, which he found to promote the autoxidation of certain sulphur compounds, has a distinct hindering effect on the propagation of flame in carbon disulphide–air near the limit.

FIG. 5.

Showing the ignition point of a 3% carbon disulphide–air mixture when some of the air is replaced by a third substance.



I desire to thank Messrs. Nobel Industries, Ltd., and particularly Mr. W. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

THE NOBEL LABORATORIES, ARDEER. [*Received, December 1st*, 1926.]

CXVII.—*The Velocity of Formation of Quaternary Ammonium Salts from Trimethylamine and Benzyl Chloride and the Three Mononitrobenzyl Chlorides.*

By HAMILTON MCCOMBIE, HAROLD ARCHIBALD SCARBOROUGH, and FREDERICK FRANCIS PERCIVAL SMITH.

IT has been shown (J., 1926, 2863) that the relative order of the velocity of saponification of the isomeric methoxybenzoic esters and of ethyl benzoate is not the same in the two alcohol–water mixtures used as solvents. This behaviour appeared to be unusual and to require further investigation.

The choice of a suitable reaction which can be followed in a wide range of solvents is almost limited to the formation or decomposition of ammonium or sulphonium salts. The reaction selected was the formation of a quaternary ammonium salt from trimethylamine and a substituted benzyl chloride. The isomeric nitrobenzyl chlorides have been used by previous investigators and were deemed to be of interest for our present purpose.

Several workers have assumed that the effect of a substituent upon the velocity of reaction will depend upon the precise mechanism by which interaction takes place; this applies equally whether the effect be a general or an alternating effect. This assumption appears to be well illustrated by the behaviour of the alkyl and aryl halides with a number of reagents. It was pointed out by Slator (J., 1909, **95**, 100) that the results fell into at least two types when a comparison was made between the velocity coefficients of a series of reactions in which an organic halide was one of the reactants; thus the results with sodium ethoxide, sodium acetoacetate, and sodium thiosulphate showed great similarities. A second type of result was obtained with dissolved oxygen and with silver nitrate. The reaction with hydrolysing reagents gave results which differed in type from both the other classes. This division into types would appear to be true even when the comparison is drawn between three isomerides. The velocity coefficients for the reaction of the nitrobenzyl chlorides with a hydrolysing reagent (Olivier, *Rec. trav. chim.*, 1922, **41**, 646), with sodium thiosulphate (Slator, *loc. cit.*), and with potassium iodide (Conant, *J. Amer. Chem. Soc.*, 1925, **47**, 488) show this difference in type (Table I).

TABLE I.

			Relative values of *k*.		
			Nitrobenzyl chlorides.		
Reagent.	Solvent.	Benzyl chloride.	*ortho.*	*meta.*	*para.*
Alkali.	Aq. alcohol.	22·6	1·06	1·28	1·00
Sodium thiosulphate.	,,	0·54	0·54	0·64	1·00
Trimethylamine.	,,	—	0·81	0·86	1·00
Potassium iodide.	Acetone.	0·14	1·32	0·57	1·00
Trimethylamine.	,,	0·98	0·55	0·80	1·00

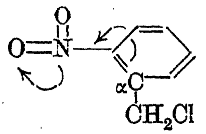
It is seen that on hydrolysis the benzyl chloride and the *m*-nitrobenzyl chloride have relatively higher velocity coefficients, whereas in the other reactions the *p*-nitrobenzyl chloride has the highest of these three. It would seem impossible to include the ortho-substituted halide in any generalisation, as the steric factor is variable and occasionally unexpected in its effects. A consideration of the results recorded in Tables I and II may be divided into two parts: first, the general effect of the nitro-group on the reactivity of the chlorine in the benzyl chloride molecule, and, secondly, the relative reactivities of the *o*-, *m*-, and *p*-nitrobenzyl chlorides.

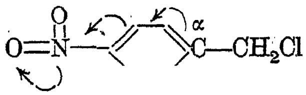
In connexion with the results obtained by Olivier (*loc. cit.*) for the hydrolysis of the nitrobenzyl chlorides, Robinson (J., 1926, 384) has suggested a mechanism based essentially upon the relative strengths of benzoic acid and the nitrobenzoic acids. Since the results obtained with potassium iodide, sodium thiosulphate, and trimethylamine differ so widely from those obtained on hydrolysis, it would appear that some other mechanism is involved.

To explain these results, the authors base their suggestions upon the relative strengths of the nitrophenols or of the nitrobenzoic acids as compared with the unsubstituted compounds. Since the substituted compounds have higher dissociation constants than the corresponding unsubstituted compounds, the general effect of the nitro-group is to give the benzene ring, as a whole, a higher affinity for a negative charge; further, they suggest that this attraction of electrons towards the nitro-group may proceed so far that the negative electronic attraction between the hydrogen and oxygen atoms may be converted into a positive repulsion between the nuclear charges of these atoms. In the event of dissociation, it is assumed that the valency electrons would be retained by the heavier nuclear charge of the oxygen atom, and the hydrogen would be thus liberated as a positive ion. If this conception is extended to the nitrobenzyl chlorides, it is seen that the nitro-group causes a movement of electrons towards itself and, as a consequence, repulsion of the nuclear charge of the chlorine atom may occur; there is, however, one essential difference, since, if the chlorine breaks away, it would be expected to do so as a negative ion, and this would necessitate the valency electrons of the carbon–chlorine union going with the chlorine atom. Thus the carbon–chlorine union in the nitrobenzyl chlorides is under a greater strain than that in the unsubstituted benzyl chloride, but this strain may be opposed by a second influence, since, if the chlorine is dissociated, the benzyl residue would become a positive ion which would be inconsistent with its greater affinity for a negative charge.

In the reactions with sodium thiosulphate and with potassium iodide, the product of the reaction is of a similar chemical nature to one of the reactants, and since no positive ion is formed by the benzyl residue, the difference in the velocity coefficients of the substituted and of the unsubstituted benzyl chlorides is to be ascribed to the strain on the carbon–chlorine union caused by the nitro-group. The reaction with trimethylamine is a special case, since in this reaction the chlorine is detached as a negative ion and the benzyl residue becomes part of the positive benzyltrimethylammonium ion, and the strain upon the carbon–chlorine union may be partly or completely neutralised by the resistance of the substituted benzyl residue to forming a part of this positive ion.

In a consideration of the alternating effect of the nitro-group, Robinson has shown (*loc. cit.*) that an electronic drift is caused in the direction of this grouping which may be represented as follows:





and that this drift will be most marked in the case of the *o*- and *p*-isomerides. Its effect will be to leave the carbon atoms marked α more positive than they were before the introduction of the nitro-group, and consequently the alternate effect will be in the same direction as the general effect.

In applying these considerations to groups other than the nitro-group, it was noted that, if the suggested electronic drifts of the general and of the alternate effects were in the same direction (*e.g.*, with the NH_2 and CH_3 groups), then

$$k_m > \text{ or } < k_p \text{ according as } k_{\text{unsubs.}} > \text{ or } < k_{\text{subs.}}.$$

In the case of the methoxy-group, the general effect is small and no generalisation is possible, and in the case of the halogens, the general and alternate effects are opposed.

Various views have been put forward to explain solvent effect; thus Cox (J., 1921, **119**, 142) suggested the formation of solvent–solute complexes, but Hawkins (J., 1922, **121**, 1170) was unable to obtain any evidence that such compounds exist. The effect due to the viscosity of the solvent has been examined by Buchböck (*Z. physikal. Chem.*, 1900, **34**, 229).

Arrhenius (*ibid.*, 1889, **4**, 226) was the first to suggest that molecules must be activated before they can enter into reaction. This energy of activation has more recently been ascribed to radiation (Lewis, J., 1914, *et seq.*) and to molecular collisions between the reacting molecules (Hinshelwood, *Phil. Mag.*, 1926, **2**, 360). The authors suggest that in the case of a reaction taking place in solution, the solvent itself activates the reacting molecules by means of its external electrical field. It is impossible to obtain a measure of this, as it is not completely expressed by the dielectric constant, by the chemical reactivity, or by the solvent power. It

TABLE II.

(p-Nitrobenzyl chloride, $k = 1$.)

Solvent.	Benzyl chloride.	Nitrobenzyl chlorides.	
		ortho.	*meta.*
Ethyl acetate	0·62	0·42	0·79
Acetone	0·97	0·55	0·80
Benzene	1·02	0·68	0·74
Ethyl benzoate	1·08	0·63	0·72
Anisole	1·32	0·70	0·71
Nitrobenzene	1·45	0·67	0·68
Ethyl alcohol	—	0·69	0·87
94·45% Alcohol–Water	—	0·69	0·85
Acetonitrile	—	0·79	0·87

might be expected that the presence of such groupings as an ethylenic linking, or of such elements as nitrogen, oxygen, or the halogens in a solvent would tend to increase the power of the solvent as an activating agent. The results recorded in Table II are in accord with these views. That the polarising action of the solvent is not its only effect, however, is shown in Table III, in which the columns headed 1, 2, 3, and 4 give respectively the relative reaction coefficients for the addition of trimethylamine to p-nitrobenzyl chloride, of ethyl iodide to triethylamine, of aniline to bromoacetophenone, and of allyl bromide to pyridine.

TABLE III.

Solvent.	1.	2.	3.	4.
Hexane	1	0·46	—	—
Ether	1·8	—	14	—
Benzene	17	17	17	17
Ethyl alcohol	108	94	680	136
Benzyl alcohol	298	332	510	—
Methyl alcohol	298	130	1020	—
Acetone	497	149	340	289
Nitrobenzene	1060	—	170	731
Acetophenone	890	—	—	595

Further consideration of the results given in Table II shows that the first six solvents stand in the order in which they decrease the value of the ratios k_m/k_p, k_p/k_o, and of $k_{\text{subs.}}/k_{\text{unsubs.}}$. These regularities are capable of explanation if it is assumed that the solvent has the power to increase or decrease the effect of the nitro-group on the halogen atom. In the ratios k_m/k_p and k_p/k_o, which depend upon the alternating effect of the nitro-group, the solvents in the given order increase the electronic drift, and since this is more powerful in the p- than in the m-position, the ratio k_m/k_p decreases.

The given range of solvents appears to influence the general effect in exactly the opposite order. Thus a range of solvents increasing the velocity of interaction of the *p*-nitrobenzyl chloride relatively to the *m*-isomeride should increase $k_{\text{subs.}}$ relatively to $k_{\text{unsubs.}}$, whereas the ratio decreases. Alcohol, acetonitrile, and anisole show yet a third effect of the solvent in that the ratios k_m/k_p and k_o/k_p are increased by these three solvents.

Dimroth (*Annalen*, 1910, **377**, 131) showed that the effect of solubility of the reactant in an intramolecular change was represented by $k \propto 1/S$, where k is the velocity coefficient and S the solubility of the starting product. It was shown that in the reaction between trimethylamine and *p*-nitrobenzyl chloride the relationship $k \propto 1/S_1S_2$ was not true (von Halban, *loc. cit.*). It appeared of interest to test the formula for the *meta*/*para* and *ortho*/*para* ratios of the nitrobenzyl chlorides. The relationship becomes $(k_m/k_p)(S_m/S_p) = \text{const.}$, since the solubility of the amine cancels out. It will be seen from Table IV that, even when the solubility ratios vary over a range of 50% and the velocity ratios over a similar range, no constant could be obtained.

TABLE IV.

	m/*p* Ratios.			*o*/*p* Ratios.		
Solvent.	100 k_m/k_p.	S_m/S_p.	Product.	100 k_o/k_p.	S_o/S_p.	Product.
Benzene	74	—	—	66·1	4·09	270
Ethyl acetate	78·7	5·65	490	41·8	3·69	154
Acetone	80·1	5·08	410	55·5	3·41	189
Ethyl benzoate	72·4	5·19	375	63·2	3·34	211
Nitrobenzene	68	4·78	325	67	3·18	212
Alcohol	86·6	3·79	320	69·5	3·20	222

EXPERIMENTAL.

The *o*- and *m*-nitrobenzyl chlorides were Kahlbaum products; the *p*-nitrobenzyl chloride was prepared by the nitration of benzyl chloride according to the method of Beilstein (*Annalen*, 1866, **139**, 337). The solvents acetone, acetonitrile, and anisole were B.D.H. products; the ethyl acetate, ethyl benzoate, and nitrobenzene were prepared in the usual manner. The trimethylamine was stored as the hydrochloride, from which the free amine was liberated, as required, by warming with concentrated aqueous potassium hydroxide. The gas was dried by passing through a series of soda-lime tubes, and absorbed immediately in the freshly-distilled solvent. The solution was standardised by titration against hydrochloric acid, a mixture of methyl-orange and sodium indigotin-sulphonate being used as indicator.

The reaction was carried out in sealed tubes, each containing 10 c.c. of the amine and 10 c.c. of the chloride solution. The tubes were filled, drained, and sealed whilst immersed in an ice-bath. Zero time was assumed to be the moment at which the tubes were placed in the thermostat, which was at 30° ± 0·1°. Usually seven tubes were used for each determination.

The ionisable chlorine was estimated gravimetrically. The tube was smashed under alcoholic silver nitrate and the solution diluted with water. This procedure ensured that all the quaternary ammonium chloride reacted with the silver nitrate, as it was found that with such solvents as nitrobenzene a mere shaking with aqueous silver nitrate was insufficient for a quantitative extraction. A slight modification was necessary in the experiments in which benzyl chloride was used: the tube was opened under water and the mixture shaken with benzene to remove unchanged benzyl chloride; the benzene was washed with small volumes of water, the wash-waters were added to the aqueous layer, and excess of silver nitrate was added. The silver chloride precipitates were weighed in a series of Gooch crucibles.

The solubilities of the nitrobenzyl chlorides (Table VIII) were determined by weighing solvent and solute into small bulbs, sealing off, and heating with shaking until solution was complete. The first reading was usually rejected; the succeeding three or four agreed within 0·1°, and this temperature was accepted as that of solution. Five determinations, with varying weights of solvent, were used in constructing a curve from which the solubility at 30° could be read off.

In the Tables V—VII, *a* represents the concentration of amine and *b* that of the benzyl or nitrobenzyl chloride expressed in g.-mol./litre.

TABLE V.

Benzyl chloride and trimethylamine in acetone.

$a = 0·1362$; $b = 0·1101$.

Time (mins.).	Wt. of AgCl.	x.	$k \times 10^4$.
73	0·1350	0·0471	698
90	0·1514	0·0528	691
135	0·1873	0·0653	695
178	0·2077	0·0725	692
210	0·2221	0·0775	685
244	0·2330	0·0813	685
310	0·2548	0·0889	702
		Mean	692

TABLE VI.

m-Nitrobenzyl chloride and trimethylamine in acetonitrile.

$a = 0·09377$; $b = 0·04490$.

Time (mins.).	Wt. of AgCl.	x.	$k \times 10^3$.
63	0·0670	0·0234	146
70	0·0717	0·0250	146
80	0·0765	0·0267	145
100	0·0844	0·0294	142
113	0·0887	0·0310	141
124	0·0927	0·0324	142
		Mean	143

It was found that the quaternary ammonium salts were almost insoluble in benzene, ethyl acetate, and ethyl benzoate, slightly soluble in acetone, and easily soluble in nitrobenzene.

TABLE VII.

Benzyl chloride and trimethylamine.

Solvent.	*a.*	*b.*	Limit *k.*	Mean *k.*
Ethyl acetate ...	0·1647	0·1994	0·00650—0·00705	0·0067
Acetone	0·1362	0·1101	0·0680 —0·0700	0·069
Benzene	0·3006	0·3465	0·00247—0·00250	0·00248
Ethyl benzoate ...	0·2165	0·1497	0·0237 —0·0254	0·0238
Anisole	0·1894	0·2012	0·0205 —0·0217	0·0212
Nitrobenzene	0·0836	0·0492	0·211 —0·221	0·218
o-Nitrobenzyl chloride and trimethylamine.				
Ethyl acetate ...	0·1392	0·1699	0·00440—0·0046	0·00452
Acetone	0·0651	0·0730	0·0388 —0·0398	0·0394
Benzene	0·1855	0·1642	0·00155—0·00163	0·00160
Ethyl benzoate ...	0·0855	0·1248	0·0133 —0·0147	0·0139
Anisole	0·2365	0·1712	0·0111 —0·0113	0·0112
Nitrobenzene	0·1153	0·0711	0·0995 —0·103	0·101
Ethyl alcohol ...	0·1552	0·0835	0·0118 —0·0124	0·0122
94·45% Alcohol	0·1330	0·0726	0·0142 —0·0149	0·0145
Acetonitrile	0·1357	0·0771	0·129 —0·132	0·130
m-Nitrobenzyl chloride and trimethylamine.				
Ethyl acetate ...	0·1572	0·1339	0·0083 —0·0087	0·0085
Acetone	0·1334	0·0635	0·0541 —0·0578	0·0568
Benzene	0·1828	0·1538	0·00167—0·00190	0·0018
Ethyl benzoate ...	0·1961	0·1344	0·0155 —0·0164	0·0160
Anisole	0·2393	0·1904	0·0111 —0·0119	0·0114
Nitrobenzene	0·1182	0·0722	0·098 —0·103	0·102
Ethyl alcohol ...	0·1798	0·0909	0·0148 —0·0157	0·0151
94·45% Alcohol	0·1330	0·0722	0·0177 —0·0184	0·0179
Acetonitrile	0·0938	0·0449	0·141 —0·146	0·143
p-Nitrobenzyl chloride and trimethylamine.				
Ethyl acetate ...	0·1572	0·1413	0·0104 —0·0113	0·0108
Acetone	0·1365	0·0627	0·0698 —0·0729	0·071
Benzene	0·1784	0·1604	0·00236—0·00250	0·0024
Ethyl benzoate ...	0·2062	0·1353	0·0214 —0·0227	0·0221
Anisole	0·2369	0·1847	0·0156 —0·0168	0·0160
Nitrobenzene	0·1167	0·0631	0·145 —0·157	0·150
Ethyl alcohol ...	0·1801	0·0881	0·0170 —0·0179	0·0175
94·45% Alcohol	0·1330	0·0695	0·0209 —0·0213	0·0210
Acetonitrile	0·0795	0·0437	0·158 —0·172	0·175

TABLE VIII.

Solubilities of the nitrobenzyl chlorides at 30°.

(G. of chloride per 100 g. of solvent.)

Solvent.	*ortho-.*	*meta-.*	*para-.*
Acetone	433	644	126·8
Benzene	304	—	74·2
Ethyl acetate	257	394	69·7
Nitrobenzene	217	326	68·2
Ethyl benzoate	171·3	266	51·2
Ethyl alcohol	26·3	30·4	8·2

One of the authors (F. F. P. S.) expresses his thanks to the Department of Scientific and Industrial Research for a grant which has enabled him to collaborate in this work.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, December 31st*, 1926.]

CXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XIII. The Nitration of Some γ-Phenylpropylamine Derivatives.*

By CHRISTOPHER KELK INGOLD and IAN STUART WILSON.

FOR reasons which will be apparent from the introductory statement of Part X (this vol., p. 250), we have studied the nitration of γ-phenylpropylammonium nitrate and of γ-phenylpropyltrimethylammonium picrate. The proportions of *m*-isomeride formed are given in the lowest line of the following table, the other numerical values being taken from previous papers (*loc. cit.*, and J., 1926, 2441) to illustrate the effect of homology.

Nitration in Nitric Acid at 0° *to* − 15°.

	$C_6H_5\cdot[CH_2]_x\cdot NH_2HX$ (primary).	$C_6H_5\cdot[CH_2]_x\cdot NMe_3\}X$ (quaternary).
$x = 1$	49%	88%
$x = 2$	12%	19%
$x = 3$	3%	5±2%

[The limits attached to the figure for the last quaternary salt arise from the circumstance that the proportion of nitrated salt which cannot be separated from the inorganic salts produced on neutralising the nitration solution is of the order of magnitude of the quantity of *m*-derivative formed; therefore, the unknown quantity of *m*-compound which may be contained in this unseparated portion cannot be neglected in comparison.]

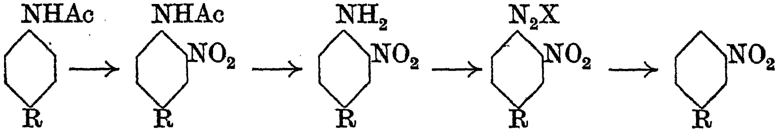
EXPERIMENTAL.

γ-Phenylpropyltrimethylammonium Picrate.—γ-Phenylpropylamine was prepared by Michaelis and Jacobi's method (*Ber.*, 1893, **26**, 2160) and purified by conversion into the oxalate. This salt (10 g.) was boiled for a few minutes with ethyl alcohol (380 c.c.) and anhydrous sodium carbonate (38 g.), and the cooled mixture treated with 41 c.c. of methyl sulphate. The reaction was completed by boiling for 2 hours, and after the addition of water the excess of methyl sulphate was destroyed and the greater portion of the alcohol was removed by distillation. The aqueous solution (250 c.c.)

was extracted twice with ether to remove tertiary bases, and, after expulsion of the dissolved ether by boiling, was mixed with a saturated solution of sodium picrate. The salt which separated crystallised from aqueous alcohol in orange-yellow prisms, m. p. 121° (Found : C, 53·2 ; H, 5·6. $C_{18}H_{22}O_7N_4$ requires C, 53·2 ; H, 5·5%).

γ-p-*Nitrophenylpropyltrimethylammonium picrate* was prepared from γ-*p*-nitrophenylpropylamine (below) by the same method (Found : C, 47·7 ; H, 4·8. $C_{18}H_{21}O_9N_5$ requires C, 47·9 ; H, 4·7%). It forms yellow prisms, m. p. 138°.

γ-m-*Nitrophenylpropyltrimethylammonium Picrate*.—This was synthesised, by the following process, from the *p*-isomeride, which was first converted into the corresponding *p*-acetamido-compound $[R = \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot \overset{+}{N}(CH_3)_3]$:



A solution of the *p*-nitro-picrate (10 g.) in concentrated hydrochloric acid (200 c.c.) was shaken with benzene to remove the picric acid and then reduced with stannous chloride (25 g.) at 100° during 0·75 hour. After dilution, the tin was removed as sulphide and the solution evaporated to dryness. The *dihydrochloride* thus obtained was acetylated by boiling with acetic anhydride (20 c.c.) and anhydrous sodium acetate. The residue obtained on evaporation to dryness was dissolved in water and the solution mixed with saturated sodium picrate solution. Very little picrate was precipitated by this means, and the solution was therefore evaporated to dryness and the residue extracted with acetone. The salt dissolved by the acetone was crystallised first from water and then from alcohol (m. p. 153°; yield 50%). The γ-p-*acetamidophenylpropyltrimethylammonium picrate* so obtained was nitrated at — 18° during 2 hours with 7·5 parts of nitric acid (*d* 1·49). The solution was allowed to warm to 0° during 15 minutes, mixed with two volumes of ice (picric acid was precipitated), and neutralised with concentrated sodium hydroxide solution (picric acid redissolved and a picrate crystallised). γ-m-*Nitro*-p-*acetamidophenylpropyltrimethylammonium picrate* separates from alcohol in prisms, m. p. 140° (Found : C, 47·9 ; H, 5·0. $C_{20}H_{24}O_{10}N_6$ requires C, 47·3 ; H, 4·8%). It was boiled gently with ethyl alcohol (40 parts) and concentrated sulphuric acid (4 parts) until the volume was reduced to one-third ; a further quantity of alcohol was then added and the boiling continued until ethyl acetate ceased to be contained in the distillate. The solution was diluted with fresh alcohol, neutralised with anhydrous sodium carbonate, and filtered, and the residue was well washed with alcohol. The combined filtrates were evaporated to a small bulk, acidified with concentrated sulphuric acid, and diazotised at 0° with a saturated solution of sodium nitrite. The solution was then heated at 100° until nitrogen ceased to be evolved, treated with excess of anhydrous sodium carbonate and sodium picrate, and evaporated to dryness. The residue was extracted with boiling acetone, and the residue obtained on evaporating the acetone was re-extracted with hot ethyl acetate, from which the m-*nitro-picrate* separated in yellow needles, m. p. 156° (Found: C, 48·2; H, 4·8. $C_{18}H_{21}O_9N_5$ requires C, 47·9; H, 4·7%). Its constitution was proved by oxidation (below).

Nitration of γ-Phenylpropyltrimethylammonium Picrate.—The picrate (5·00 g.) was added during 1 hour to 25 c.c. of nitric acid ($d^{10°}$ 1·49) at − 15°, and the mixture was then kept at or below this temperature for 1 hour and thereafter allowed to warm to 5° during 0·5 hour. Ice was added, and the solution rendered alkaline with concentrated sodium hydroxide solution at − 10°. The nitro-derivative was collected, and crystallised from methyl alcohol and ethyl acetate until no further crops of pure *p*-isomeride (total 47%) could be obtained. All the solutions were then evaporated to dryness and the residues extracted in a Soxhlet apparatus with acetone; the residues from the acetone were again extracted with ethyl acetate, the final product being washed with a very little water. The yield was 49%, making a total yield of mononitro-products equal to 96%. The mixture of isomerides (Found: C, 48·3, 48·4; H, 5·0, 4·9. Calc.: C, 47·9; H, 4·7%) was oxidised in 84% yield to nitrobenzoic acids by permanganate, and the *p*- and *m*-acids were estimated by separation as described in previous parts of this series (*p*-, 66%; *m*-, 6·5%).

Two parallel experiments in which the pure *p*- and *m*-nitro-picrates were separately oxidised to the corresponding nitrobenzoic acids by means of permanganate gave yields amounting to 81% and 80%, respectively. This shows that there is no selective destruction of the *m*-isomeride during the oxidation mentioned in the preceding paragraph, and that the proportion of *m*-nitrobenzoic acid represents the proportion of *m*-nitro-picrate in the mixture oxidised.

On this assumption, there is 3·2% of *m*-isomeride in the 96% of mononitration product accounted for. The total formed could not be more than 7·2%, and is very unlikely to be so much. The proportion of *p*-isomeride is $47 + 0{\cdot}49 \times 66 \pm 2 =$ about 81%.

Nitration of γ-Phenylpropylamine.—The base was run through a capillary tube into 7·5 parts of nitric acid (*d* 1·49) at − 15°. Two hours were allowed for the nitration and the nitric acid solution was then warmed to 5° and mixed with ice.

γ-p-*Nitrophenylpropylammonium nitrate* (48·5%) was obtained in needles, m. p. 200°, from the crystalline mixture of nitrates by crystallisation from water. The corresponding *chloride* forms prisms, m. p. 165° (Found: C, 50·2; H, 6·2. $C_9H_{13}O_2N_2Cl$ requires C, 49·9; H, 6·0%). Small amounts of neutral and acid oxidation products were removed from the combined liquors by extraction with ether, and the remainder of the mononitration product (40%) was then isolated by basifying it with sodium hydroxide and again extracting it (Found for the corresponding nitrates: C, 45·0; H, 5·1. Calc.: C, 44·4; H, 5·4%). This was oxidised in 66% yield to a mixture of nitrobenzoic acids, the *p*- and *m*-acids in which were estimated by separation as before (*p*-, 55%; *m*-, 6%). The pure *p*-acid, on oxidation under the same conditions, gave *p*-nitrobenzoic acid in 67% yield.

The proportions of *m*- and *p*-isomerides calculated on the total mononitration product are therefore *m*-, 2·7%; *p*-, 73%.

The authors desire to thank the Royal Society for a grant which has covered part of the cost of this work.

THE UNIVERSITY, LEEDS. [*Received, January* 12*th*, 1927.]

CXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XIV. The Directive Action of Groups of the Form* $-CH_2 \cdot SO_2 \cdot R$ *in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD, EDITH HILDA INGOLD, and FLORENCE RUTH SHAW.

THE characteristic actions of a pole and of a dipole in controlling the position of substitution of a benzene derivative having been established in broad outlines by recent investigations (see below), a number of subsidiary influences required elucidation. The following will be considered.

(i) *Influence of neutral * atoms in modifying the orienting effect of a charged atom.* The nitro-group contains a neutral as well as a negative oxygen atom, and when comparing the electron-affinities of the nitro- and ammonium salt groups, as measured by their meta-directive effects in the nitration of phenylnitromethanes and benzylamine salts, Baker and Ingold (J., 1926, 2462; this vol., p. 261) assumed that the influence of the neutral

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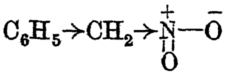
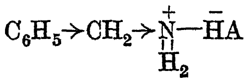
* Here, as previously, the term "neutral" is used relatively and is not intended to exclude atoms carrying the feeble charges represented by δ+ and δ−.



$$C_6H_5\rightarrow CH_2\rightarrow \underset{\underset{O}{\|}}{\overset{+}{N}}-\overset{-}{O}$$

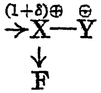
(meta, 50%)



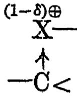
$$C_6H_5\rightarrow CH_2\rightarrow \underset{\underset{H_2}{\|}}{\overset{+}{N}}-\overset{-}{HA}$$

(meta, 49%)

atoms attached to the positive ends of the dipoles would be small in comparison with the effect of the dipoles themselves. This is doubtless correct in the cases considered, but it is nevertheless conceivable that atoms of greatly differing electron-affinities (*e.g.*, carbon and fluorine) might allow their electrons to be attracted by a charged atom in such different degrees as to modify the effective charge on that atom, if not largely, at least to an appreciable extent :



$$\rightarrow\underset{\underset{F}{\downarrow}}{\overset{(1+\delta)\oplus}{X}}-\overset{\ominus}{Y}$$



$$\underset{\underset{-C<}{\uparrow}}{\overset{(1-\delta)\oplus}{X}}-\overset{\ominus}{Y}$$

This effect has been searched for and has now been detected.

(ii) *Influence of a second charged atom : Compensation by the more distant end of a dipole.* The smaller *m*-directive action observed in phenylnitromethanes and benzylamine salts of the above types, as compared with the benzyltrialkylammonium ion (meta, 85—88%) (Goss, Ingold, and Wilson, J., 1926, 2440; Goss, Hanhart, and Ingold, this vol., p. 250), has been attributed (J., 1926, 2445) to partial compensation by electron-repulsion from the more distant negative end of the dipole. In the above examples, however, the negative charges are carried by different kinds of atoms, and for a strict demonstration of this principle it is desirable (see below) that atoms of the same kind should be used, and only the total charges varied. This method is employed in the present work, and the effect of varying the compensating charge in the ratio 3/2 is recorded.

(iii) *Damping action of external electron-shells in positively charged atoms.* The diminution in the *m*-directive influence of a positively charged atom separated from the nucleus by an increasing number of neutral atoms (Part X, *loc. cit.*) shows that each group of electrons through which the electron-strain is transmitted exerts an appreciable damping action :

$$\underset{100\%}{Ph{\cdot}\overset{+}{N}Me_3} \qquad \underset{88\%}{Ph{\cdot}CH_2{\cdot}\overset{+}{N}Me_3} \qquad \underset{19\%}{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3}$$

$$Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3$$

5±2% of *m*-nitro-derivative.

Since the positive electricity with which the strain originates resides at the *nucleus* of the charged atom, a similar damping action may be expected to arise during the passage of the effect through the successive shells of electrons belonging to the charged atom itself, and this consideration enables us to forecast the relative orienting influences of equivalent ionic charges carried by different atoms. Phosphorus and sulphur atoms in the combined state possess a group of eight electrons external to the ten which correspond with the ten in the combined nitrogen atom; arsenic, selenium, and iodine atoms contain groups additional to those present in phosphorus and sulphur. It follows that phenyl- and benzyl-phosphonium and -thionium ions should exhibit weaker *m*-directive action than the analogous phenyl- and benzylammonium ions; that phenyl and benzyl sulphoxides (dipole) should show weaker *m*-orientation than the corresponding aromatic nitro-compounds; that aromatic arsonium and selenonium salts should show weaker *m*-reactivity than the comparable phosphonium and thionium salts, and so forth.* Of course, apart from this screening action of the outer electrons, the magnitude of the effect escaping from a charged atom will depend on the ionic charge; whence it follows, also, that aromatic sulphones (double dipole) should show stronger *m*-orienting action than the corresponding sulphoxides (unit dipole). The testing of such predictions as these is necessarily a lengthy task, but we are already able to advance evidence showing that the nitrogen and sulphur atoms stand in the anticipated order.

Results.

In the experimental section a comparative study is recorded of the nitration of a series of benzylsulphonyl compounds of the general formula $C_6H_5{\cdot}CH_2{\cdot}SO_2{\cdot}R$. The results, so far as they bear upon the three topics raised, may be summarised as follows:

Nitration of Benzylsulphonyl Compounds, $C_6H_5{\cdot}CH_2{\cdot}SO_2{\cdot}R$ *in Nitric Acid* ($d^{18°}$ 1·494) *at* − 10° *to* − 5°.

Group R	CH_3	NH_2				OH	Cl
Meta (%)	30	31				14	51
Group R		$NHMe$	$NHEt$	NMe_2	NEt_2	OMe	
Meta (%)		29	28	28	25	32	

Although based for the most part on tolerably consistent triplicate determinations (for details, see Table, p. 832), these figures can only be regarded as approximate; nevertheless, it appears probable that they place the various groups in the correct order, excepting possibly in the cases of some of those which gave closely similar values.

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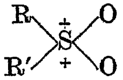
* The same principles, applied to the fractional dipoles discussed in the following paper, show that $C_6H_5{\cdot}SiCl_3$ and $C_6H_5{\cdot}CH_2{\cdot}SiCl_3$ should exhibit weaker *m*-orientation than $C_6H_5{\cdot}CCl_3$ and $C_6H_5{\cdot}CH_2{\cdot}CCl_3$ respectively, and we propose to study these and the other comparisons mentioned.

Discussion of Results.

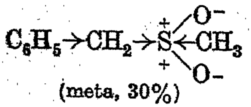
The above group of compounds was selected for study because it appeared likely to yield evidence regarding the three anticipated subsidiary influences already alluded to.

According to Sugden, Reed, and Wilkins (J., 1925, **127**, 1525) the sulphone group contains two semi-polar double linkings, so that the structure of sulphones must be represented thus:



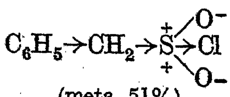
and there is ample chemical evidence that these semi-polar double linkings are not easily depolarised. The static neutral character of methanesulphones ($\cdot CH_2\cdot SO_2$), contrasted with the acid nature of nitromethanes ($\cdot CH_2\cdot NO_2$; one true double bond), shows—if we accept the theory (E. H. Ingold, J., 1923, **123**, 1717, *et seq.*) that triad tautomerism represents internal addition to an unsaturated centre—that there is no real or potential unsaturated linking in the sulphone group. Similarly, the non-formation of sulphonamides from sulphonic esters and aqueous ammonia, in contrast to the ready production of carboxylamides from carboxylic esters, accords with the assumed structural difference ($-SO_2\cdot OMe$, no double bond; $-CO\cdot OMe$, one double bond) if, as Gane and Ingold suggested (J., 1926, 11), aldehyde-ammonia addition is the first stage in the formation of carboxylamides from esters. For these and other reasons, we may regard the valency-octet of sulphur in sulphones as fixed for most reactions, and the charge on the core of the atom (nucleus + 10 electrons) as fixed also.

(i) *Influence of neutral atoms.* Of the simpler available groups, R (R′ = benzyl), the greatest disparity was to be expected (p. 814) between $-CH_3$ and $-F$, but we have not troubled to prepare benzylsulphonyl fluoride because the readily obtained chloride gave a perceptibly higher meta-value than the methyl sulphone:



$$C_6H_5{\rightarrow}CH_2{\rightarrow}\overset{+\nearrow O^-}{\underset{+\searrow O^-}{S}}{\leftarrow}CH_3$$

(meta, 30%)



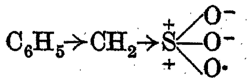
$$C_6H_5{\rightarrow}CH_2{\rightarrow}\overset{+\nearrow O^-}{\underset{+\searrow O^-}{S}}{\rightarrow}Cl$$

(meta, 51%)

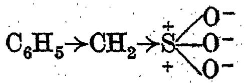
On the other hand, all the other instances investigated (excepting R = OH—see below) yielded values differing only slightly from that given by the methyl sulphone, and from this we may conclude that the fractional charges set up by the varying electron affinities of neutral atoms are insignificant in comparison with such integral ionic charges as the charge inherent in the sulphur atom of a sulphone, excepting in the case of strongly electro-polar atoms such as those of the halogen family.

(ii) *Influence of charged atoms.* Since the meta-value for R = F should be at least as great as that for R = Cl, it will be evident from the above table that $-OH$ falls out of its place in the possible sequence $NH_2 < OH < F$. A rough estimate of the meta-value expected for R = OH [made by noting the value obtained for the methyl ester (R = OMe) and the relationship between the figure for the amide ($R = NH_2$) and those for the substituted amides (R = NHMe, NMe_2, etc.)] would be about 35%, which does lie between the limits set by $R = NH_2$ and Cl; but the observed value (14%) falls far short of this.

The difference, however, is readily interpreted on the grounds that sulphonic acids are strong acids and may be assumed to be almost completely ionised in solution; in other words, the case of benzylsulphonic acid corresponds, not with R = OH, but with R = O′, the depression of the meta-value representing the effect of introducing a third negatively charged oxygen atom in addition to the two already present in the sulphone group. We can call to mind no clearer proof than this of the compensating action of the more remote end of a dipolar group: *



(meta, *ca.* 35%)



(meta, 14%)

(iii) *Influence of the sulphur electrons.* If the meta-value 35% approximately represents the effect of the two-fold dipole in the sulphone group, the unit dipole contained in a similarly situated sulphoxide group must correspond with a much smaller meta-value, and although we have as yet made no experiments with benzylalkylsulphoxides, we feel sure that under comparable conditions they would not yield more than small proportions (*e.g.*,

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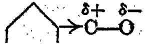
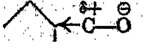
* The *op*-substitution of benzoic acid in alkaline solution (Lossen, D.R.-P. 146174), in contrast to its *m*-substitution in acid media, is regarded (see following paper) as an illustration of the reversal of the effect of a *fractional* charge by an *integral* charge of opposite sign situated at a greater distance:

(*meta-*)   (*ortho-para-*).

It follows that benzenesulphonic acid should not show the same marked difference of behaviour under the two conditions, since (unlike benzoic acid) the free acid would be nearly as strong an electrolyte as its salts.

5—10%) of *m*-isomeride. Comparison with the value (50%) established for the unit dipole in the analogously situated nitro-group (p. 814) shows that the effect of a positive ionic charge on sulphur must suffer relatively greater loss within the atom itself than is the case with nitrogen.

EXPERIMENTAL.

(A) *Preparation of Benzylsulphonyl Compounds.*

Benzylmethylsulphone, $C_7H_7{\cdot}SO_2{\cdot}CH_3$.—Benzylsulphonyl chloride (50 g.) was reduced with zinc dust (24 g.) and boiling alcohol (1000 c.c.) as described by Fromm and Palme (*Ber.*, 1906, **39**, 3312), and the neutralised liquid (70 g. of anhydrous sodium carbonate were used) evaporated to dryness under reduced pressure. The residue was extracted with hot alcohol (1000 c.c.), and the filtered solution evaporated to dryness, also under diminished pressure. The residue from this evaporation was dissolved in 200 c.c. of water, and the filtered solution shaken with 25 c.c. of methyl sulphate at 40° until crystals began to appear. Sodium hydroxide (40 c.c. of 8*N*-solution) was gradually added and the shaking continued until the temperature began to fall; the mixture was then heated to 75°, shaken for a further 15 minutes, and allowed to cool. Yield, 21 g.; m. p. 123—125°. The specimen used for nitration was crystallised first from aqueous alcohol and then from chloroform–ligroin.

Benzylsulphonamide and the Sulphonalkylamides.—The unsubstituted amide was prepared as recommended by Johnson and Ambler (*J. Amer. Chem. Soc.*, 1914, **36**, 380) and purified by crystallisation from water. Benzylsulphonmethylamide, $C_7H_7{\cdot}SO_2{\cdot}NHMe$, prepared by dissolving the sulphonyl chloride in 33% aqueous methylamine and boiling off most of the excess of the base, separated from aqueous alcohol or from ethyl acetate–ligroin in laminæ, m. p. 108—109° (Found: S, 17·7. Calc.: S, 17·3%). Johnson and Ambler (*loc. cit.*) obtained the same substance along with the dimethylamide (below) by methylation of the simple amide.

Benzylsulphonethylamide, $C_7H_7{\cdot}SO_2{\cdot}NHEt$, was similarly prepared, excepting that the excess of ethylamine was neutralised with hydrochloric acid, and crystallised first from aqueous methyl alcohol below the ordinary temperature and finally from ether–ligroin, from which it was obtained as leaflets, m. p. 65—66° (Found: S, 16·0. $C_9H_{13}O_2NS$ requires S, 16·1%).

Benzylsulphondimethylamide, $C_7H_7{\cdot}SO_2{\cdot}NMe_2$, was obtained by means of aqueous dimethylamine, and crystallised first from dilute methyl alcohol and then from chloroform–ligroin; it formed large, thin plates, m. p. 101° (Found: S, 15·9. Calc.: S, 16·1%).

Benzylsulphondiethylamide, $C_7H_7\cdot SO_2\cdot NEt_2$, prepared by dissolving the chloride in excess of pure diethylamine and pouring the solution into dilute sulphuric acid, crystallised from ether–ligroin below 0° in leaflets, m. p. 29° (Found: S, 14·2. $C_{11}H_{17}O_2NS$ requires S, 14·1%).

Benzylsulphonic Acid and its Methyl Ester.—The sodium salt of the acid prepared by Johnson and Ambler's method (*loc. cit.*) was crystallised three times from water. The *methyl* ester was prepared by boiling the chloride with a slight deficit of methyl-alcoholic sodium methoxide for 15 minutes, after which the suspension was cooled and mixed with water, and the crystalline precipitate, which contained a little unaltered chloride, was collected and ground for 1·5 minutes with aqueous ammonia (*d* 0·880). The mixture was diluted with water, and the solid was collected, washed with an abundance of cold water, dried, and crystallised from ether; large, lustrous prisms then separated, m. p. 61—62° (Found: C, 52·0; H, 5·2; S, 17·3. $C_{10}H_8O_3S$ requires C, 51·6; H, 5·4; S, 17·2%). On boiling with water for 5 minutes, complete hydrolysis takes place.

Benzylsulphonyl Chloride.—This was prepared as recommended by von Pechmann (*Ber.*, 1873, **6**, 534). The specimen used for nitration was crystallised twice from chloroform–ligroin.

(B) *Nitration of Benzylsulphonyl Compounds and Estimation of the* m-*Isomeride: General Method.*

It was found possible to effect the smooth mononitration of all the substances investigated except one (the diethylamide) under the same set of conditions. The proportion of nitric acid ($d^{18°}$ 1·494) was 1 kg. per g.-mol. of substance, the latter being added in small portions at the uniform rate of 0·2 g. per minute to the rapidly stirred acid at − 10° to − 5°. The mixture was warmed to 0° during 1 hour and then mixed with ice. The method of isolating and separating the nitration product varied with the different examples, but in all cases excepting the methylsulphone, the sulphonic acid, and the diethylamide the pure *m*-isomeride was isolated; in the case of the methylsulphone, it was obtained in an impure condition and in the case of the sulphonic acid it was isolated as a derivative.

For the estimation of the *m*-isomeride, the method of oxidation by permanganate and separation of the nitrobenzoic acids (Baker and Ingold, *loc. cit.*; Goss, Hanhart, and Ingold, *loc. cit.*) was employed, and although the yields of mixed nitrobenzoic acids were not quantitative (they were mostly in the neighbourhood of 80—85%) it was possible to correct for any small disparities in the percentage conversions of the different isomerides by noting the yields obtained on oxidation of the separated isomerides and of mixtures of them of different composition,* precautions being taken to keep the conditions of oxidation comparable in each group of experiments. In most experiments, partial separation of the original nitration product was effected before oxidation was resorted to.

(C) *Details relating to Individual Cases.*

(*a*) *Benzylmethylsulphone.* — (i) *Qualitative separation.* The nitration product was obtained in a total yield of 97·6%, of which 70·3% was precipitated on the addition of ice and 27·3% was extracted by chloroform from the neutralised filtrate. The precipitated part (Found: C, 45·1; H, 4·0. Calc.: C, 44·7; H, 4·2%) had m. p. 90—140°, and 1·00 g., crystallised from 40 c.c. of benzene, yielded 0·57 g. of a product, m. p. 160—165°, which, crystallised from alcohol, yielded (in two fractions) 0·48 g., m. p. 167—168°. Further crystallisation did not change this m. p., and since oxidation yielded *p*-nitrobenzoic acid, m. p. 234—236° unpurified (mixed m. p. 235—236°), this compound must be p-*nitrobenzylmethylsulphone* (Found: C, 44·4; H, 4·5; N, 6·7. $C_8H_9O_4NS$ requires C, 44·7; H, 4·2; N, 6·5%). The product contained in the mother-liquors, on crystallisation from alcohol and from ethyl acetate–alcohol, gave needles (0·25 g.), m. p. 105—106°, which, although consisting mainly of m-*nitrobenzylmethylsulphone* (Found: C, 44·3; H, 4·5; N, 6·6%), still contained a small proportion of the *p*-isomeride. This was shown by oxidation and separation of the nitrobenzoic acids. The extracted part of the nitration product (Found: C, 44·6; H, 4·2%) had m. p. 75—105°; after three crystallisations from ethyl acetate–alcohol, it gave needles, m. p. 85—87°, consisting (as was shown by oxidation to the nitrobenzoic acids) mainly of o-*nitrobenzylmethylsulphone* (Found: C, 44·5; H, 4·6; N, 6·6%) but contaminated with an appreciable quantity of the *m*-isomeride.

(ii) *Estimation of* m-*isomeride* (Expt. 14). The yield of nitration product was 99·9%, of which 85·7% was precipitated (Found: C, 44·9; H, 4·0. Calc.: C, 44·7; H, 4·2%) and 14·2% extracted

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* If $100x$, $100y$, and $100z$ represent the percentage conversions of *o*-, *m*-, and *p*-nitro-isomerides, respectively, and if three mixtures give yields of mixed nitrobenzoic acids amounting to $100Y_1$, $100Y_2$, and $100Y_3$, these products having compositions represented respectively by $100o_1$, $100m_1$, $100p_1$%; $100o_2$, $100m_2$, $100p_2$%; and $100o_3$, $100m_3$, $100p_3$% of *o*-, *m*-, and *p*-nitro-acids, then x, y, and z are given by:

$$x\begin{vmatrix} M_1P_11 \\ M_2P_21 \\ M_3P_31 \end{vmatrix} = y\begin{vmatrix} P_1O_11 \\ P_2O_21 \\ P_3O_31 \end{vmatrix} = z\begin{vmatrix} O_1M_11 \\ O_2M_21 \\ O_3M_31 \end{vmatrix} = \begin{vmatrix} O_1M_1P_1 \\ O_2M_2P_2 \\ O_3M_3P_3 \end{vmatrix}$$

where $O_1 = o_1Y_1, O_2 = o_2Y_2 \ldots M_1 = m_1Y_1 \ldots P_3 = p_3Y_3$.

with chloroform (Found: C, 44·6; H, 4·2%). The precipitated part on oxidation gave nitrobenzoic acids in 80% yield (*M*, by titration, 167; benzoic acid, by sublimation, nil), which on separation gave 48·9% * of *p*-nitrobenzoic acid, m. p. 234—235°, mixed m. p. 235—236°, and 28·5% * of *m*-nitrobenzoic acid, m. p. 134—138°, mixed m. p. 139—140°. The crude recovered *o*-nitrobenzoic acid (containing *m*-acid) had m. p. 133—143°, mixed m. p. 143—145°, and the total recovery of separated acids was 98·8%. The extracted portion gave nitrobenzoic acids (*M*, 166; benzoic acid, nil) in >74% yield, the exact figure being unknown, as a little of the solution was accidentally lost. Separation gave 9·2% of *p*-acid having m. p. 225—230° (mixed m. p. 230—233°) and 35·7% of *m*-acid, m. p. 133—136° (mixed m. p. 138—141°). The recovered *o*-acid (containing a little *m*-acid) had m. p. 133—137°, mixed m. p. 135—140°.

(Expt. 15.) *p*-Nitrobenzylmethylsulphone was isolated in 34·5% yield, and the residue divided by crystallisation into two fractions amounting to 51·4% and 14·1% of the whole, the total yield in this experiment being quantitative. The first fraction, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 168; benzoic acid, nil), and these, on separation, gave 9·5% of *p*-acid, m. p. 232—234°, mixed m. p. 234—235°, and 49·4% of *m*-acid, m. p. 130—136°, mixed m. p. 138—140°. The second fraction gave an 81% yield of nitrobenzoic acids (benzoic acid, nil) which on separation yielded 9·4% of *p*-acid, m. p. 224—228°, mixed m. p. 230—234°, and 35·9% of *m*-acid, m. p. 131—134°, mixed m. p. 137—139°.

(Expt. 16.) The yield of nitration product was 98·4%, and from this 38·4% of the theoretical (39·0% of the actual) yield of the pure *p*-isomeride was isolated. The residues, on oxidation, gave nitrobenzoic acids in 84·6% yield (*M*, 167; benzoic acid, nil) which on separation yielded 5·8% of *p*-acid, m. p. 225—230°, and 50·5% of *m*-acid, the precipitated part of which (42·6%) had m. p. 136—137° and mixed m. p. 140°, whilst the part extracted with ether (7·9%) had m. p. 120—130°, mixed m. p. 135—138°.

(Calculations.) From these three experiments we find: para $= 0·858 \times 48·9 + 0·142 \times 9·2 = 43·3\%$, $34·5 + 0·514 \times 9·5 + 0·141 \times 9·4 = 40·7\%$, $39·0 + 0·610 \times 5·8 = 42·6\%$; meta $= 0·858 \times 28·4 + 0·142 \times 35·7 = 29·5\%$, $0·514 \times 49·4 + 0·142 \times 35·9 = 30·6$, $0·610 \times 50·5 = 30·8\%$, the disparities in the oxidation conversions being negligible in this case. The mean values are, therefore, para, 42·2%; meta, 30·3%; ortho (by difference), 27·5%.

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* These, and all other yields of *p*- and *m*-nitrobenzoic acids recorded in this section are corrected for the solubility of the *p*-acid and the *m*-barium salt (Baker and Ingold, *loc. cit.*).

(*b*) *Benzylsulphonamide.*—(i) *Qualitative separation.* Part of the nitration product (28·1%) was precipitated on the addition of ice, and this consisted mainly of *p*-nitrobenzylsulphonamide (Mohr, *Annalen*, 1883, **221**, 218) which was purified by crystallisation from hot water and obtained as clusters of small needles, m. p. 203—204° (Found: C, 39·3; H, 3·8. Calc.: C, 38·9; H, 3·7%). The same substance was obtained by the action of aqueous ammonia on *p*-nitrobenzylsulphonyl chloride. On oxidation, it yielded only *p*-nitrobenzoic acid, m. p. 234—235° (unpurified). The nitric acid solution, on complete evaporation with water, deposited first further quantities of the same isomeride and later the crude *m*-compound as plates, m. p. 150—160°. On recrystallisation, these yielded long, felted needles, m. p. 161°, consisting of pure *m*-nitrobenzylsulphonamide (Purgotti and Monti, *Gazzetta*, 1900, **30**, [ii], 254), as was proved by oxidising them to pure *m*-nitrobenzoic acid, m. p. 139—140° (unpurified), mixed m. p. 139—140°. The same compound was obtained from *m*-nitrobenzylsulphonyl chloride by treatment with aqueous ammonia. It is much more soluble in water than the *p*-amide.

(ii) *Estimation of the* m-*isomeride* (Expt. 21). The precipitated portion of the nitration product corresponded with 27·8% of the theoretical yield and had m. p. 160—190° (Found: C, 38·5; H, 3·9. Calc.: C, 38·9; H, 3·7%). On oxidation, nitrobenzoic acids (*M*, 166; benzoic acid, nil) were obtained in 83·2% yield, and these on separation gave 82·6% of *p*-acid, m. p. 230—232°, mixed m. p. 231—234°, and *m*-acid which was obtained in two portions, the first (6·7%, precipitated) having m. p. 137—139°, mixed m. p. 140°, and the second (2·2%, extracted with ether) m. p. 125—135°, mixed m. p. 135—140°. The dilute nitric acid solution was evaporated, with several additions of water, to dryness in a vacuum; the residue was not weighed, but, as there was no opportunity for loss, was taken to correspond with 72·2% (Found: C, 38·3; H, 3·7%). Nitrobenzoic acids were obtained in 74·4% yield (*M*, 167; benzoic acid, 0·2%), and their separation gave *p*-acid, m. p. 228—232°, mixed m. p. 230—234° (28·7%), precipitated *m*-acid, m. p. 137—139°, mixed m. p. 140° (30·0%), and extracted *m*-acid, m. p. 125—132°, mixed m. p. 138° (7·5%).

(Expt. 22.) The precipitated portion of the nitration product (28·1%) on crystallisation from water yielded 21·4% of *p*-nitrobenzylsulphonamide (m. p. 203—204°). The residue obtained by evaporating the nitric acid solution was crystallised in successive fractions from water, yielding 9·7% of *p*-amide (m. p. 203—204°), 0·6% of *p*-amide (m. p. 202—204°), and 6·2% of impure *m*-amide (m. p. 150—160°) which, after a further crystallisation, yielded

5·2% of pure *m*-amide (m. p. 161°). All mother-liquors were now combined and evaporated, and the residues (60·7% instead of 63·1%) oxidised as usual. The nitrobenzoic acids (yield, 81·3%; *M*, 166; benzoic acid, nil) on separation gave *p*-acid, m. p. 228—230°, mixed m. p. 232—234° (13·1%); *m*-acid (precipitated), m. p. 136—137°, mixed m. p. 140° (28·5%); and *m*-acid (extracted), m. p. 125—131°, mixed m. p. 136—140° (10·1%).

(Expt. 25.) The precipitated part of the nitration product was crystallised from water, and the filtrate was combined with the dilute nitric acid solution and evaporated, with additions of water, in a vacuum. The *o*- and *m*-amides were extracted with hot water from the sparingly soluble *p*-amide, and were allowed to crystallise after evaporation of the solution to a small bulk; the final filtrate was evaporated to dryness. The yield of *p*-amide (m. p. 203—204°) was 35·6%, of "crystallised mixture" (Found: C, 38·6; H, 3·7. Calc.: C, 38·9; H, 3·7%) 58·7%, and of "evaporated mixture" 5·6% (loss 0·1%). Two independent oxidations of the crystallised mixture gave nitrobenzoic acids in 83·2 and 82·5% yields, respectively, and an average sample of the combined products (*M*, 167; benzoic acid, nil) on separation gave *p*-acid (7·1%), m. p. 220—230°, mixed m. p. 229—232°; *m*-acid (precipitated, 39·6%), m. p. 137°, mixed m. p. 140°; *m*-acid (extracted, 8·6%), m. p. 125—130°, mixed m. p. 135—138°. The nitrobenzoic acids (*M*, 165; benzoic acid, 0·3%) obtained from the evaporated mixture yielded no *p*-acid, and 32·6% of *m*-acid, m. p. 125—135°, mixed m. p. 137—140°, and the *o*-acid recovered had m. p. 130—135° (unpurified), 143—145° (after one crystallisation from chloroform), mixed m. p. 145°.

(Expt. 26.) By a method similar to that used in Expt. 22 the *p*-amide (23·9%, m. p. 203—204°, plus 12·2%, m. p. 202—204°, plus 2·0%, m. p. 200—204°) and *m*-amide (11·6%, m. p. 158—161°) were partly separated, the crop of *m*-amide being obtained by crystallisation from 50% alcohol, and the residues oxidised (yield 83·3%) to nitrobenzoic acids. Separated, these gave 6·2% of *p*-acid, m. p. 225—230°, mixed m. p. 230—232°, and 40·9% of *m*-acid, of which the bulk (precipitated) had m. p. 137—138° (mixed m. p. 140°) and the remainder (extracted), m. p. 124—135° (mixed m. p. 136—139°).

(Calculations.) The isolated *p*-amide on oxidation gave *p*-nitrobenzoic acid in (*a*) 86·0, (*b*) 86·6% yields, and the *m*-amide yielded the *m*-acid in (*a*) 78·1, (*b*) 79·0% yields. A mixture of 0·500 g. of each amide gave mixed acids in 83·2% yield, and these on separation yielded 52·8% of *p*-acid, m. p. 230—233°, and 47·2% of *m*-acid, of which 37·6% had m. p. 136—138° and the remainder

(9·6%) m. p. 124—130°. From these experiments, and the data obtained in Expts. 25 (crystallised mixture) and 26, it is calculated that the percentage conversions of the *o*-, *m*-, and *p*-amides are 87·2, 78·5, and 86·3%, respectively. These figures being used, Expt. 21 gives para, 0·278 × 81·8 + 0·722 × 27·7 = 42·7%; meta, 0·278 × 10·8 + 0·722 × 39·7 = 31·7%; ortho, 25·6%: Expt. 22 gives para, 31·7 + 0·631 × 12·7 = 39·7%; meta, 5·2 + 0·631 × 40·8 = 31·0%; ortho, 29·3%: Expt. 25 gives para, 35·6 + 0·587 × 6·8 = 39·6%; meta, 0·587 × 50·6 + 0·057 ×35 = 31·6%; ortho, 28·8%: Expt. 26 gives para, 38·1 + 0·503 × 6·0 = 41·1%; meta, 11·6 + 0·503 × 43·2 = 33·3%; ortho, 25·6%. Since Expt. 26 does not agree well with the other three, it is excluded from the following mean values: Para, 40·7%; meta, 31·4%; ortho (by difference), 27·9%.

(*c*) *Benzylsulphonmethylamide.*—(i) *Qualitative separation.* The precipitated portion of the nitration product, after crystallisation successively from methyl alcohol, ethyl acetate, and chloroform, gave needles, m. p. 143—145° (Found: C, 41·4; H, 4·4. $C_8H_{10}O_4N_2S$ requires C, 41·7; H, 4·4%), which consisted of p-*nitrobenzylsulphonmethylamide*, since oxidation with permanganate yielded only *p*-nitrobenzoic acid, m. p. 232—234° (unpurified), mixed m. p. 234°. The same methylamide was prepared from the *p*-nitro-chloride and aqueous methylamine. In another experiment, the whole nitration product was extracted with ethyl acetate after neutralisation, and the bulk of the *p*-isomeride allowed to crystallise from this solvent. The mother-liquors on evaporation gave a residue which, on slow crystallisation from methyl alcohol, yielded stellate clusters of needles, m. p. 106—107° (Found: C, 41·4; H, 4·5%). This compound was identified as m-*nitrobenzylsulphonmethylamide*, since, on oxidation with permanganate, it yielded only *m*-nitrobenzoic acid, m. p. 137—140° (unpurified), mixed m. p. 139—140°. It was also prepared from *m*-nitrobenzylsulphonyl chloride and aqueous methylamine.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 32). The diluted nitric acid solution was evaporated in a vacuum, without collection of the precipitated nitro-compounds, and the product oxidised as usual. The nitrobenzoic acids (yield, 76·8%; *M*, 166·5; benzoic acid, nil) gave 42·2% of *p*-acid, m. p. 228—231°, mixed m. p. 230—234°; 21·1% of precipitated *m*-acid, m. p. 134—137°, mixed m. p. 140°; and 7·3% of extracted *m*-acid, m. p. 120—133°, mixed m. p. 134—138°.

(Expt. 36.) The precipitated nitration product (yield 98·4%) was extracted with ethyl acetate after neutralisation (Found: C, 41·6; H, 4·6. Calc.: C, 41·7; H, 4·4%), and after separation of 32·6% (calculated on the actual yield) of the *p*-isomeride, the remaining amide was oxidised in 82·2% yield to nitrobenzoic acids which on separation gave 10·4% of *p*-acid, m. p. 234—235°, 33·7% of precipitated *m*-acid, m. p. 134—137°, mixed m. p. 139—140°, and 73% of extracted *m*-acid, m. p. 123—136°, mixed m. p. 137—140°.

(Expt. 37.) The product isolated by complete evaporation was separated by crystallisation, giving 29·5% of *p*-methylamide of m. p. 138—141°, 6·2% of m. p. 138—140° and 1·7% of m. p. 137—139°, and 6·8% of *m*-methylamide, m. p. 99—101°. A mixture of the second and third specimens of *p*-compound gave only *p*-nitrobenzoic acid, m. p. 230—234°, and the separated *m*-compound yielded only *m*-nitrobenzoic acid, m. p. 137—139°, on oxidation. Oxidation of the residues was effected in 83·5% yield, and the nitrobenzoic acids (*M*, 166; benzoic acid, 0·9%) on separation gave 11·0% of *p*-acid, m. p. 220—230°, mixed m. p. 227—232°; 29·5% of precipitated *m*-acid, m. p. 134—135°, mixed m. p. 141°; and 9·0% of extracted *m*-acid, m. p. 122—130°, mixed m. p. 135—140°.

(Calculations.) The isolated *p*- and *m*-methylamides gave corresponding nitrobenzoic acids in 85·2 and 80·5% yields, respectively, and it is calculated from Expts. 36 and 37 that the *o*-compound would give about 84·0% under the same conditions. Hence, para = 41·5%, 32·6 + 0·674 × 10·2 = 39·5%, 37·4 + 0·558 × 11·3 = 43·7%; meta = 29·5%, 0·674 × 42·3 = 28·5%, 6·8 + 0·558 × 39·8 = 29·0%. The mean values are: Para, 41·5%; meta, 29·0%; ortho (by difference), 29·5%.

(*d*) *Benzylsulphonethylamide*.—(i) *Qualitative separation.* The precipitated portion of the nitration product was rubbed with a little cold methyl alcohol, and the sparingly soluble portion crystallised from this solvent in needles, m. p. 110—111°. These consisted of p-*nitrobenzylsulphonethylamide* (Found: C, 44·2; H, 5·1. $C_9H_{12}O_4N_2S$ requires C, 44·3; H, 4·9%), since on oxidation they yielded only *p*-nitrobenzoic acid, m. p. 230—234° (unpurified). The same substance was also prepared from *p*-nitrobenzylsulphonyl chloride and aqueous ethylamine. m-*Nitrobenzylsulphonethylamide* was isolated in small amount by fractional crystallisation of the residues from dilute methyl alcohol. It formed stellate bunches of needles, m. p. 90—91° (Found: C, 44·0; H, 5·2%), and on oxidation gave only *m*-nitrobenzoic acid, m. p. 137—139° (unpurified), mixed m. p. 139—140°. The same isomeride was prepared from *m*-nitrobenzylsulphonyl chloride and aqueous ethylamine.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 42). The residue from the diluted and evaporated solution (Found: C, 44·2;

H, 5·1%) was oxidised in 78·4% yield to nitrobenzoic acids (*M*, 167; benzoic acid, 0·9%) which on separation (after removal of the benzoic acid) gave 42·8% of *p*-acid, m. p. 225—230°, mixed m. p. 228—232°; 20·6% of precipitated *m*-acid, m. p. 135—137°, mixed m. p. 140°; and 7·1% of *m*-acid, m. p. 125—132°, mixed m. p. 135—140°, which was extracted with ether.

(Expt. 45.) The *p*-ethylamide (36·6%), m. p. 108—110°, was separated by means of methyl alcohol, and the residues were oxidised to the mixed acids (yield, 79·0%; *M*, 165·5; benzoic acid, nil) which on separation gave 10·9% of *p*-acid, m. p. 224—228°, mixed m. p. 227—231°, 33·7% of precipitated *m*-acid, m. p. 134—139°, mixed m. p. 140°, and 10·4% of *m*-acid, m. p. 124—130°, mixed m. p. 136—140°, extracted with ether.

(Expt. 47.) Preliminary separation gave 32·4% of *p*-amide, m. p. 108—111°, 5·7% of m. p. 107—109°; and 8·1% of *m*-amide, m. p. 86—89°, and 0·6%, m. p. 85—87°. The residues yielded nitrobenzoic acids (yield, 81·0%; *M*, 167; benzoic acid, nil), which on separation gave 6·8% of *p*-acid, m. p. 228—230°, mixed m. p. 230—234°, and 36·7% of *m*-acid, of which 28·5% (precipitated) had m. p. 135—138° and 8·2% had m. p. 125—130° (mixed m. p.'s 140° and 138—139°, respectively).

(Calculations.) The isolated *p*- and *m*-ethylamides gave the corresponding nitrobenzoic acids in 80·4 and 79·1% yields, respectively, and the yields obtained from mixtures were all of this order. Hence the experiments cited give para: 42·8%, $36·6 + 0·634 \times 10·9 = 43·6\%$, $38·1 + 0·532 \times 6·8 = 41·9\%$; meta: 27·5%, $0·634 \times 44·1 = 28·0\%$, $8·7 + 0·532 \times 26·7 = 28·2\%$, the means being: para, 42·8%; meta, 27·9%; ortho (by difference), 29·3%.

(*e*) *Benzylsulphondimethylamide.*—(i) *Qualitative separation of isomerides.* The precipitated part of the nitration product, crystallised first from methyl alcohol and then from ethyl alcohol, gave leaflets, m. p. 167°, consisting of p-*nitrobenzylsulphondimethylamide* (Found: C, 44·6; H, 4·7. $C_9H_{12}O_4N_2S$ requires C, 44·3; H, 4·7%). On oxidation by permanganate, it yielded only *p*-nitrobenzoic acid, m. p. 233—234° (unpurified), and it was identical with the substance obtained by dissolving *p*-nitrobenzylsulphonyl chloride in aqueous dimethylamine. m-*Nitrobenzylsulphondimethylamide* was obtained from the mother-liquors as leaflets, m. p. 116—119°, which was not depressed by admixture with a specimen, m. p. 118—119°, obtained from the pure *m*-nitro-chloride (Found: C, 44·3; H, 5·1%). The substance was oxidised by permanganate to *m*-nitrobenzoic acid, m. p. 137—140° (unpurified), mixed m. p. 139—140°.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 52). The whole nitration product obtained by dilution and evaporation in a vacuum (Found: C, 44·0; H, 4·4%) was oxidised in 76·7% yield to mixed acids (*M*, 166; benzoic acid, 0·2%) which on separation gave 44·5% of *p*-acid, m. p. 225—233°, mixed m. p. 230—235°, and 27·5% of *m*-acid, of which the bulk (precipitated) had m. p. 138°, mixed m. p. 141°, and the remainder, extracted with ether, m. p. 120—130°, mixed m. p. 136—139°.

(Expt. 55.) The *p*-derivative was isolated in 31·1% yield, m. p. 164—166°, and the residues oxidised in 70·1% yield to mixed acids, which on separation gave 16·7% of *p*-acid, m. p. 230—232°, mixed m. p. 234—235°, and 39·6% of *m*-acid, of which 30·0% had m. p. 133—137°, mixed m. p. 139—140°, and 9·6% had m. p. 125—130°, mixed m. p. 135—138°.

(Expt. 57.) A series of crystallisations yielded 33·7% of the *p*-compound, of which 26·7% had m. p. 164—166° and 7·0% m. p. 163—165°, and 10·6% of *m*-compound, of which 10·3% had m. p. 114—117° and the remainder m. p. 112—116°. The residues (55·0% instead of 55·7%) on oxidation gave nitrobenzoic acids (yield 74·7%) which on separation gave 17·9% of *p*-nitrobenzoic acid, m. p. 220—230°, mixed m. p. 230—234°, and 34·2% of *m*-acid, of which the bulk (precipitated) had m. p. 132—137°, mixed m. p. 139—140°, and the remainder m. p. 120—130°, mixed m. p. 136—139°.

(Calculations.) Independent oxidations of the *p*-compound gave 78·9 and 79·4% yields, and of the *m*-compound 73·8 and 75·6% yields, whence from Expt. 57 the *o*-isomeride should give a 73·3% yield under the same conditions. Hence the data given lead to para: 43·8%, $31·1 + 0·689 \times 15·6 = 41·8\%$, $33·7 + 0·557 \times 16·8 = 43·0$; meta: 28·1%, $0·689 \times 39·8 = 27·5\%$, $10·6 + 0·557 \times 34·3 = 29·7\%$. The mean values are therefore: para, 42·9%; meta, 28·4%; ortho (by difference), 28·7%.

(*f*) *Benzylsulphondiethylamide.*—Difficulty was experienced with the nitration of this substance owing to its tendency to oxidise, but in one experiment (63) it was shown that nitration occurs in the *m*-position to a substantial extent. The substance (1·500 g., this small amount being used owing to the difficulty of keeping the temperature down when oxidation sets in if larger quantities are employed) was nitrated at − 10° to − 5° as usual, and the solution, after being kept for 10 minutes, was mixed with ice and sodium carbonate solution and extracted with ether. The extract was concentrated without drying, and when the bulk was small, water was added and the solution was boiled to expel the remainder of the ether and treated with permanganate. The mixed acids (yield, 53·7% calculated as nitrobenzoic acids on the basis of the diethylamide used for nitration) lost 8·6% of their weight at 100°, and the residual mixed nitro-acids (*M*, 166) consisted, as was found by separation, of 47·2% of *p*-nitro-acid, m. p. 220—225°, mixed m. p. 228—233°; 25·1% of *m*-acid, of which the bulk (precipitated) had m. p. 133—135°, mixed m. p. 138—141°, and the remainder (extracted) had m. p. 115—125°, mixed m. p. 132—139°; and (by difference) 27·7% of *o*-acid. The recovered *o*-acid, crystallised once from chloroform, had m. p. 140—146°, mixed m. p. 144—145°. These figures, namely, para, 47·2%; meta, 25·1%; ortho, 27·7%, are regarded as an approximation to the proportions of the nitro-diethylamides originally formed.

(*g*) *Benzylsulphonic Acid.*—This substance has been nitrated by Böhler (*Annalen*, 1870, **154**, 55), who, however, obtained no individual substance, and by Mohr (*loc. cit.*), who showed that the *p*-nitro-derivative was the principal product and that the *o*-isomeride was also formed; the *m*-isomeride was not detected.

(i) *Qualitative examination.* The solution obtained by adding sodium benzylsulphonate to nitric acid under the usual conditions was evaporated in a vacuum after the addition of water, and the residue was crystallised from aqueous alcohol; sodium *p*-nitrobenzylsulphonate (Purgotti and Monti, *loc. cit.*) was then obtained. On oxidation it yielded only *p*-nitrobenzoic acid, m. p. 232—234° (unpurified). The mother-liquors were evaporated, and the residues were washed with a little aqueous alcohol, which removed part of the very soluble sodium *o*-nitrobenzylsulphonate, and treated with phosphorus oxy- and penta-chlorides at 90° for 0·5 hour. The sulphonyl chlorides, collected after decomposition with water of the excess of phosphorus chlorides, when crystallised from chloroform–ligroin, gave *m*-nitrobenzylsulphonyl chloride as plates, m. p. 101°, which in some fractions were mixed with prisms from which they could be mechanically separated. On hydrolysis, they yielded Purgotti and Monti's *m*-nitrobenzylsulphonic acid (*loc. cit.*).

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 72). The well-dried nitration product was converted into the mixed chlorides with phosphorus penta- and oxy-chlorides at 90°, and the chlorides transformed by ammonia in dry ether into the amides, which were oxidised. The nitrobenzoic acids (yield, 74·6% calculated on the original sodium benzylsulphonate; *M*, 166; benzoic acid, nil) on separation gave *p*-acid (53·9%), m. p. 227—233°, mixed m. p. 230—235°, and *m*-acid (12·5%), the greater portion of which had m. p. 135—137° (mixed m. p. 139—140°) and the remainder m. p. 125—131° (mixed m. p. 136—140°). The recovered *o*-acid (33·6%; loss nil) after one crystallisation from chloroform had m. p. 140—143°, mixed m. p. 143—146°.

(Expt. 73.) The same method being followed initially, the nitro-chlorides (93·7% yield) were prepared, and crystallised from chloroform–ligroin; 29·3% of the *p*-nitro-chloride (prisms, m. p. 89—90°) were then separated. The mother-liquors yielded a small crop (2·2%) of the *m*-derivative (plates, m. p. 99—100·5°). The remaining material was converted into amides and oxidised in 76·0% yield (calculated on the nitro-chlorides) to mixed acids (*M*, 167; benzoic acid, nil), which on separation gave 33·7% of *p*-acid, m. p. 225—231°, mixed m. p. 230—235°, and 16·0% of *m*-acid, of which 11·0% (the precipitated part) had m. p. 135—137°, mixed m. p. 139—140°, the remainder having m. p. 125—131°, mixed m. p. 135—138°.

(Expt. 74.) The method was the same as in Expt. 72, and the separation yielded 54·6% of *p*-acid, m. p. 230—231°, mixed m. p. 231—234°, and 12·8% of *m*-acid (isolated altogether), m. p. 130—132°, mixed m. p. 137—140°.

(Expt. 75.) The method of Expt. 73 being adopted initially, the chlorides were separated, yielding 23·7% of *p*-chloride (m. p. 89—90°) and 3·1% of *m*-chloride (m. p. 98—100°), and the residues converted into amides, which on partial separation yielded 9·8% of *p*-amide (m. p. 200—203°). The final residues on oxidation gave nitrobenzoic acids (yield, 70·7%; *M*, 166; benzoic acid, 0·5%), which on separation yielded 29·7% of *p*-acid, m. p. 225—230°, mixed m. p. 230—234°, and 14·6% of *m*-acid, of which the bulk (precipitated) had m. p. 130—136°, mixed m. p. 139—140°, and the remainder (extracted) m. p. 120—130°, mixed m. p. 136—139°. The recovered *o*-acid, after one crystallisation from chloroform, had m. p. 141—143°, mixed m. p. 143—145°.

(Calculations.) From the previously determined oxidation-conversions of the amides, the following values are calculated: para = 53·2%, $29·3 + 0·685 \times 33·1 = 52·0\%$, 54·0%, $33·5 + 0·634 \times 29·2 = 52·0\%$; meta = 13·6%, $2·2 + 0·685 \times 17·4 = 14·1\%$, 13·9%, $3·1 + 0·634 \times 15·8 = 13·1\%$. Thus, the mean values are: para, 52·8%; meta, 13·7%; ortho (by difference), 33·5%.

(*h*) *Methyl Benzylsulphonate.*—(i) *Qualitative separation of isomerides.* Almost the whole of the nitration product was precipitated, on the addition of ice, as an oil which soon solidified. *Methyl* p-*nitrobenzylsulphonate* was readily separated by grinding the mixture with ether and crystallising the undissolved portion from ethyl acetate–ligroin, from which it separated in small, hard cubes, m. p. 113° (Found: C, 41·7; H, 3·8. $C_8H_9O_5NS$ requires C, 41·6; H, 3·9%). On oxidation by permanganate, it was converted almost quantitatively into *p*-nitrobenzoic acid, m. p. 234—235°

(unpurified). Probably hydrolysis precedes oxidation, since boiling with water for a short time converts the ester into the free sulphonic acid and methyl alcohol. By crystallising the part which dissolved in ether from ethyl acetate–ligroin, methyl *m*-nitrobenzylsulphonate was obtained as thin, rhomboidal leaflets, m. p. 99—100° (Purgotti and Monti, *loc. cit.*, record m. p. 77°), and a further quantity of the same isomeride was obtained from the mother-liquors of the *p*-compound by mechanical separation of the crystals (Found: C, 41·2; H, 3·9%). The orientation was proved by boiling with water, evaporating the neutralised solution of the sulphonic acid to dryness, and digesting the residue with phosphorus pentachloride and oxychloride at 90° for a few minutes; *m*-nitrobenzylsulphonyl chloride (m. p. 100—101°) was then obtained.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 83). The precipitated nitration product (yield 94%) was hydrolysed by boiling with water and the nitrosulphonic acids were converted into their amides as in the preceding series of experiments, and oxidised in that form. The mixed acids gave 47·0% of *p*-acid, m. p. 210—220°, mixed m. p. 220—230°, and 28·0% of *m*-acid, m. p. 127—130°, mixed m. p. 135—140°.

(Expt. 84.) The nitration product was extracted with ethyl acetate (yield 95%) and treated as in the preceding experiment. The nitrobenzoic acids gave 42·3% of *p*-acid, m. p. 225—231°, mixed m. p. 228—234°, and 31·2% of *m*-acid, of which 25·9% (precipitated) had m. p. 137—139°, mixed m. p. 139—140°, and the remainder (extracted) m. p. 122—129°, mixed m. p. 136—138°.

(Expt. 87.) The *p*-nitro-derivative was partly separated from the nitration product by means of ether and ethyl acetate (29·0% having m. p. 113°, and 4·3% having m. p. 110—113°), and the residues were converted into amides and oxidised. The acids gave 13·2% of *p*-acid, m. p. 230—232°, mixed m. p. 234—235°, and 48·1% of *m*-acid, of which 37·9% had m. p. 138—139°, mixed m. p. 140°, and the remainder had m. p. 125—130°, mixed m. p. 136—137°.

(Calculations.) Using the oxidation data for the amides, we have para $= 45·7\%, 41·0\%, 33·3 + 0·667 \times 12·7 = 41·8\%$; meta $= 29·9\%, 33·5\%, 0·667 \times 50·5 = 33·7\%$, and the means are: para, 42·9%; meta, 32·4%; ortho (by difference), 24·7%.

(i) *Benzylsulphonyl Chloride.*—(i) *Qualitative separation.* The nitration product was completely precipitated on addition of ice, and the bulk of the *m*-nitro-derivative was readily separated as leaflets, m. p. 100—101° (compare Purgotti and Monti, *loc. cit.*), by crystallisation from chloroform–ligroin (4 : 1 by vol.) (Found: C, 36·1; H, 2·8%). Its identity was shown by conversion into the *m*-amide and by oxidation to *m*-nitrobenzoic acid. p-*Nitrobenzylsulphonyl chloride* was obtained from the mother-liquors as large, inclined prisms, m. p. 90° (Found: C, 36·1; H, 2·7. $C_7H_6O_4NClS$ requires C, 35·7; H, 2·6%). On oxidation with permanganate it yielded only *p*-nitrobenzoic acid, m. p. 230—234° (unpurified), and on treatment with ammonia gave the *p*-nitro-amide.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 92). The precipitated nitration product (yield 96·9%) (Found: C, 35·7; H, 2·8. Calc.: C, 35·7; H, 2·6%) was crystallised from 1·5 parts by weight of chloroform mixed with one-quarter of its volume of ligroin; 38·4% (calculated on the yield *isolated*) of pure *m*-compound, m. p. 100—101°, then separated. The residues, on conversion into the amides and on oxidation gave nitrobenzoic acids (*M*, 166; benzoic acid, nil) which, when separated, were found to consist of 53·2% of *p*-acid, m. p. 222—230°, mixed m. p. 230—234°; 20·5% of *m*-acid, m. p. 133—135°, mixed m. p. 138°; and 26·3% of *o*-acid (by difference).

(Expt. 93.) The whole product was converted into amides and oxidised to mixed acids (*M*, 167; benzoic acid, nil) which on separation gave 36·7% of *p*-acid, m. p. 220—230°, mixed m. p. 230—232°, and 45·9% of *m*-acid, of which 30·0% had m. p. 136—137°, mixed m. p. 140°, and 15·9% had m. p. 120—130°, mixed m. p. 135—139°.

(Expt. 96.) Fractional crystallisation from chloroform–ligroin containing gradually increasing proportions of ligroin gave 39·8% of *m*-chloride, m. p. 99·5—101°, 3·0% having m. p. 99—100°, and 0·3% having m. p. 97—99°, together with 9·1% of *p*-chloride, m. p. 88—90°, and 0·2% having m. p. 87—89°. The residues, on oxidation after conversion into amides, gave nitrobenzoic acids (yield, 80·0%; *M*, 166; benzoic acid, nil) which, when separated, yielded 49·5% of *p*-acid, m. p. 224—232°, mixed m. p. 230—234°, and 17·0% of *m*-acid, of which 10% had m. p. 134—138°, mixed m. p. 140°, and 7% had m. p. 125—130°, mixed m. p. 136—139°.

(Calculations.) By the method already illustrated, the above data gave para: $0·616 \times 52·2 = 32·1\%$, 34·8%, $9·3 + 0·476 \times 48·7 = 32·5\%$; meta: $0·616 \times 22·1 = 52·0\%$, 48·6%, $43·1 + 0·476 \times 18·4 = 51·9\%$. The means, neglecting Expt. 93, are: para, 32·3%; meta, 52·0%; ortho (by difference), 15·7%. The means, including Expt. 93, are: para, 33·1%; meta, 50·8%; ortho (by difference), 16·9%.

(D) *Summary of Results.*

The following tabular summary is appended for convenience in reference:—

Nitration of Benzylsulphonyl Compounds by Nitric Acid (d^{18° 1·494) *at* − 10° *to* − 5°.

R in directing group, $CH_2·SO_2·R$.	Isomerides formed (%).				
	Para.	Mean.	Ortho.	Meta.	Mean.
CH_3	43·3 40·7 42·6	42·2	27·5	29·5 30·6 30·8	30·3
NH_2	42·7 39·7 39·6	40·7	27·9	31·7 31·0 31·6	31·4
NHMe	41·5 39·5 43·7	41·5	29·5	29·5 28·5 29·0	29·0
NHEt	42·8 43·6 41·9	42·8	29·3	27·5 28·0 28·2	27·9
NMe_2	43·8 41·8 43·0	42·9	28·7	28·1 27·5 29·7	28·4
NEt_2	47·2	47·2	27·7	25·1	25·1
OH (doubtless ionised)	53·2 52·0 52·0	52·8	33·5	13·6 14·1 13·1	13·7
OMe	45·7 41·0 41·8	42·9	24·7	29·9 33·5 33·7	32·4
Cl	32·1 34·8 32·5	33·1	16·9	52·0 48·6 51·9	50·8

The figures recorded in the last column are rounded in the abridged table given in the introduction.

THE UNIVERSITY, LEEDS.

[*Received, December* 16*th*, 1926.]

CXX.—*The Nature of the Alternating Effect in Carbon Chains. Part XV. The Directive Action of Some Groups of the Form* –CR′R″·COR *in Aromatic Substitution.*

By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

WHEN two atoms having corresponding electronic systems in the combined state, but different nuclear charges, are directly united, it is to be expected that the electrons concerned in the union will be more strongly attracted by the more powerful positive nucleus. Thus, carbon and oxygen in the combined state both possess

10 electrons, and their nuclear charges are in the ratio 6 : 8;* hence the electrons of the bond C—O will be more under the influence of the oxygen than of the carbon nucleus. In other words, the oxygen atom will have more than a half-share in these shared electrons, and so on the whole it will be feebly negatively charged. Similarly, the carbon atom, possessing less than a half-share in the same pair of electrons, will on the whole be feebly positively charged: $\overset{\delta+}{C}-\overset{\delta-}{O}$. The electric moment of this fractional dipole will, of course, be very small, but in a double bond, where the electrons are assumed to be more loosely held, the separation of ± charges consequent on an unequal nuclear attraction should be greater and the effects traceable to dipolar character correspondingly enhanced.† Thus it follows that so-called non-polar (4-electron) double bonds, such as the carbonyl bond, in which there is reason to suspect an unequal sharing of the electrons, should display to a small, but possibly detectable, extent those properties which are so strikingly characteristic of the semi-polar (2-electron) double bond and depend on the creation of an electrical field.

$$\text{(I.)}\quad -\overset{+}{N}\overset{\rightarrow}{=}\overset{-}{O} \qquad\qquad -\overset{\delta+}{C}=\overset{\delta-}{O}\quad \text{(II.)}$$

The capacity of the semi-polar double linking (I) for producing *m*-substitution, when its positive end is separated from the benzene nucleus by a saturated carbon atom, is well illustrated by the large degree of *m*-substitution observed in the nitration of phenylnitromethane derivatives (Baker and Ingold, J., 1926, 2462; this vol., p. 261); it has been confirmed by the study of benzylsulphonyl compounds (see Part XIV).

Probably the *m*-orientation effects observed in benzoyl compounds (*e.g.*, benzaldehyde, acetophenone, benzoic acid and its esters) are to be attributed, in part at least, to the occurrence of the fractional dipole (II) in the resting state of the carbonyl group, but in these cases other mechanisms are possible, depending on the alternation of single with double linkings. In phenylacetyl compounds, however, such mechanisms are excluded, and any *m*-nitration, beyond the 3% observed in the case of toluene,‡ must arise

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* The screening effect of the inner pairs of electrons will tend to increase the effective disparity, which will also be somewhat influenced by more distant electronic and nuclear charges.

† The permanent fractional dipole moments should be in the order $C{=}O > C{=}N$ and $C-F > C-O > C-N$ in the absence of poles and other powerful disturbances.

‡ For reasons given previously (J., 1926, 2462), toluene is taken as the standard of reference in the comparisons represented by:

$C_6H_5\cdot CH_2\leftarrow X$	$C_6H_5\cdot CH_2-H$	$C_6H_5\cdot CH_2\rightarrow Y$
(meta<3%)	(meta = 3%)	(meta>3%)

from the permanent dipole. We have therefore studied the nitration of ethyl phenylacetate and are able to show that it forms approximately 9% of *m*-nitro-derivative (IV). To confirm the matter, we have also examined the nitration of ethyl phenylmalonate,* in which the electron-attraction in the side-chain would be expected to be about twice as great, and in this case we find 20% of *m*-derivative (V).

The value for ethyl phenylacetate (IV) may be contrasted with that previously recorded for phenylnitromethane (III):

$C_6H_5{\cdot}CH_2{\cdot}NO_2$	$C_6H_5{\cdot}CH_2{\cdot}CO_2Et$	$C_6H_5{\cdot}CH(CO_2Et)_2$
(meta, 50%)	(meta, 9%)	(meta, 20%)
(III.)	(IV.)	(V.)

EXPERIMENTAL.

Nitration of Ethyl Phenylacetate.—Radziszewski (*Ber.*, 1869, **2**, 209; 1870, **3**, 648) nitrated this substance and established the formation of the *o*- and *p*-nitro-derivatives.

The ester was run slowly into 6 vols. of nitric acid (*d* 1·50) at 0° and the product was kept at 0° for a further 4 hours, then mixed with ice, and basified with potassium hydroxide. The precipitated nitro-products were collected, washed with cold water, and dried in ethereal solution, to which the ethereal extract of the mother-liquor was added. After analysis, the mixed nitro-compounds were oxidised to nitrobenzoic acids, in which the proportion of *m*-isomeride was determined either by titration (Baker, this vol., p. 565) or by separation (Baker and Ingold, *loc. cit.*).

(Expt. 12.) From 5·350 g. of the ester, 6·174 g. (92%) of nitro-derivatives (Found: C, 57·3; H, 5·4. Calc.: C, 57·4; H, 5·3%) were obtained; a further 6% of the material was accounted for as acid by-products formed by oxidation or hydrolysis. The yield of nitrobenzoic acids was 95% (Found: *M*, 165·6. Calc., 167). On titration, 1·2374 g. required 73·68 c.c. of 0·01029*N*-baryta for the neutralisation of the *m*-acid, corresponding with 0·1266 g. of *m*-nitrobenzoic acid, which when corrected becomes 0·110 g., or 9·3%.

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* The choice of these compounds for study requires some explanation. Benzyl alkyl ketones were ruled out owing to probable disturbances arising from the presence of enols of the type $C_6H_5{\cdot}CH{:}C(OH){\cdot}R$; phenylacetic and phenylmalonic acids should give higher proportions of *m*-derivative than their respective esters *if substitution were to occur exclusively in the undissociated forms*, but, since only a small effect was being sought for, there was no guarantee that the contrary influence of ionisation (preceding paper) would be negligible; the same is true of the influence of alkyl groups in ketones such as $C_6H_5{\cdot}CMe_2{\cdot}COR$; consequently the esters examined belong to one of the few classes of compounds suitable to our purpose.

(Expt. 13.) The yield from 10·00 g. was 12·038 g. (96%) (Found: C, 57·3; H, 5·6%), and partial separation prior to oxidation of the unseparated part was effected as follows. An average sample (5·044 g.) was crystallised from ethyl alcohol, yielding 1·038 g. of ethyl *p*-nitrophenylacetate, m. p. 62°, and the residues from the mother-liquor were again crystallised from a small quantity of the same solvent, giving 0·382 g. of the same isomeride, m. p. 60—62° (total, 1·42 g. = 28·2%). From these fractions, by oxidation, *p*-nitrobenzoic acid, m. p. 234° (unpurified; either alone or mixed with a genuine specimen), was obtained in 87% yield. 3·390 G. of the unseparated residues were similarly oxidised in 87·4% yield to nitrobenzoic acids, and on acidification of the alkaline solution 0·667 g. of *p*-nitrobenzoic acid, m. p. 234°, mixed m. p. 234°, crystallised and was collected. Extraction with ether gave 1·680 g. of mixed acids (benzoic acid, 1·1%), 1·500 g. of which, on separation, gave a further 0·262 g. of *p*-nitrobenzoic acid (solubility correction, 0·025 g.) and two fractions of *m*-acid, one of which (0·178 g.) had m. p. 128° and the other (0·139 g.) m. p. 123°, with previous softening in each case (barium salt solubility correction, 0·045 g.). Since these m. p.'s are lower than are usually observed for *m*-acid isolated in similar separations of artificial mixtures, the two fractions were crystallised from ethyl acetate–ligroin, giving 0·152 g. of pure *m*-acid, to which the barium salt solubility correction must be added together with half the weight of the impure residues. Hence the original nitration product contained: para, $28 + 20 + 10 = 58\%$; meta, $9·5 \pm 2·5\%$; ortho (by difference), $32·5 \pm 2·5\%$.

The figure for the *p*-isomeride was confirmed by an independent nitration (yield 91%, analysis correct, yield on oxidation 93%), which gave para, 59%.

Nitration of Ethyl Phenylmalonate.—The ester (Found: C, 65·4; H, 6·5. Calc.: C, 66·0; H, 6·8%) was prepared by thermal decomposition of ethyl phenyloxaloacetate, which was obtained by condensing ethyl phenylacetate with ethyl oxalate (Wislicenus, *Annalen*, 1888, **246**, 315).

(Expt. 23.) The ester was run slowly into 6 vols. of nitric acid (*d* 1·49) at − 15° to − 10° at the rate of 1 g. per hour, and after being kept for a further hour at the same temperature the mixture was poured on to ice, nearly neutralised with potassium hydroxide, and then completely neutralised with sodium carbonate. The nitration product, a yellow oil, was extracted with ether (Found: C, 54·2; H, 5·1. Calc.: C, 55·5; H, 5·4%) and oxidised with permanganate, and the nitrobenzoic acids were isolated in the usual manner (yield, 90%; *M*, 165·3). 0·4633 G. required 60·96 c.c. of 0·01029*N*-barium hydroxide to neutralise the *m*-acid, corresponding with 0·1065 g., which when corrected becomes 0·0935 g., of this isomeride, that is, 20·2%.

Another portion of the mixed acids after removal of the benzoic acid (1·8%) by sublimation was treated as in Expt. 13, and gave 47% of *p*-acid and 21 ± 5% of *m*-acid; *o*-acid (by difference), 32 ± 5%.

(Expt. 25.) The yield of nitro-compounds from 3·623 g. was 4·161 g. (90%) (Found: C, 54·5; H, 5·4%), which on oxidation gave 0·333 g. of *p*-nitrobenzoic acid (crystallised from the aqueous solution) and 1·151 g. of mixed acids (extracted with ether) (*M*, 168). The extracted portion (0·979 g.) gave 0·142 g. (crystallised) of *m*-nitrobenzoic acid, m. p. 135°, mixed m. p. 140°, and 0·049 g. (extracted with ether), m. p. 115°, mixed m. p. 128—130°. The *p*-acid was accidentally lost before weighing. For the original nitration product, meta = 18%.

Summary.—The above results are collected together in tabular form:

Nitration of Ethyl Phenylacetate and Ethyl Phenylmalonate in Nitric Acid (d 1·5).

Side-chain.	Temp. (mean).	Proportions by separation (%) (corrected for solubilities). *Para*-.	*Meta*-.	% *Meta*- (by estimation).	Mean % *meta*-.
$-CH_2\cdot CO_2Et$	± 0°	58, 59	9·5	9·3	9
$-CH(CO_2Et)_2$	−12·5	47	18, 21	20·2	20

We desire to thank the Royal Society for defraying part of the expense incurred in this investigation.

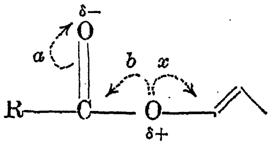
THE UNIVERSITY, LEEDS. [*Received, December 21st,* 1926.]

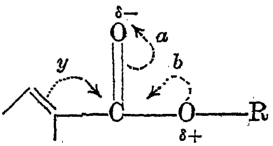
CXXI.—*The Nature of the Alternating Effect in Carbon Chains. Part XVI. The Directive Action of Some Groups of the Form* –COR *in Aromatic Substitution.*

By KENNETH ERNEST COOPER and CHRISTOPHER KELK INGOLD.

IN Part V (J., 1926, 1310), Ingold and Ingold considered the diminution in the *op*-directive power of a phenoxyl oxygen atom arising from its attachment to a carbonyl group (R·CO·OPh) and attributed the effect to the establishment of a weak electrovalency between the carboxyl oxygen atoms, thus adapting a previous theory (Smedley, J., 1909, 95, 231) of the structure of the carboxyl group. Expressed in terms of electron-strain transmission, the conception (I) was that the process (*b*), actuated by (*a*), competes with the process (*x*) to which the *op*-directing action of the group is due; or, in other words, that the charge $\delta+$, set up by (*a*) and (*b*) together, works against the repulsion of electrons towards the nucleus:

(I.)





(II.)

At first sight it might appear to follow that the *m*-directive power of a benzoyl carbonyl-group should be decreased by its attachment to a hydroxylic or ethereal oxygen atom (Ph·CO·OR) for a precisely similar reason (II): the demand created by process (*a*) can be supplied, not only by (*y*) leading to *m*-substitution, but also by (*b*), which therefore works against *m*-substitution. At least it seems that there can be no escape from this conclusion for any theory which regards the "conjugation" of the carbonyl group with the nucleus as the sole cause of its *m*-directive effect.

On the other hand, if the view (this vol., p. 833) be adopted that the action of the carbonyl group in benzoyl compounds (to illustrate by this example) arises largely from permanent electron-strain (J., 1926, 2442, 2463; this vol., pp. 813–815) set up by the fractional dipole in the resting state of the carbonyl group, then, whilst the conclusion represented by (I) remains (for the charge $\delta+$ created by strains *a* and *b* must necessarily oppose *op*-substitution), that represented by (II) becomes inverted. For each of the bonds between carbon and oxygen represents a fractional dipole (arising from the greater electron-attraction of the stronger nucleus,—see the preceding paper), the group as a whole being represented $—\overset{\delta+}{\mathrm{C}}\ \overset{\delta-}{\mathrm{O}_2}—$; and the processes (*a*) and (*b*) merely transfer electricity from one oxygen atom to the other, leaving unchanged the total negative electrification on the two taken together, and leaving unchanged also the total positive electrification on the carbon atom to which both are attached. Thus the dipole in $—\overset{\delta+}{\mathrm{C}}\ \overset{\delta-}{\mathrm{O}_2}—$ is two-fold, the smaller separation of charges in C—O being *added* to the larger separation in C=O (compare Part XV), so far as concerns the total charge on the common carbon atom; that is to say, the attachment of ethereal or hydroxylic oxygen should *enhance* the *m*-directing effect of the carbonyl group. Thus the examination of benzoyl compounds is capable of furnishing definite information as to the type of theory which should be adopted.

The main recorded observations bearing on the point are those of Camps (*Arch. Pharm.*, 1901, **240**, 1), who obtained 55% of *m*-derivative from acetophenone by nitration in nitric acid below 0°, and of Holleman (*Rec. trav. chim.*, 1899, **18**, 267; *Z. physikal. Chem.*, 1899, **31**, 79), who, under similar conditions, obtained 80% of *m*-compound from benzoic acid. Experience of the former reaction has shown the essential correctness of the estimate, and we have closely confirmed Holleman's result for the latter. These facts clearly find their most consistent interpretation in the permanent-strain hypothesis (above), but we have supplemented the evidence thus furnished by a series of experiments designed to determine the relative actions of the groups $-CH_3$, $-NH_2$, $-OH$, $-Cl$ in association with a carbonyl group attached to the benzene nucleus.

According to the conjugative mechanism (above), a series of groups, CR_3, NR_2, OR, Cl, should stand in the same order, as regards their power of competing with phenyl in supplying electrons to the carbonyl group, as they do in regard to their power of furnishing electrons, by an identical mechanism, to a directly attached benzene ring (in $CPhR_3$, $NPhR_2$, etc.), when *op*-substitution results. This order is known and is given by $N>O>Cl>C$, the atom with the most active lone-electrons heading, and that with none terminating, the series. Hence the order of the composite groups should be *

$$\xleftarrow{\text{increasing } m\text{-directive power}}$$
$$\cdot CO\cdot CH_3 > CO\cdot Cl > CO\cdot OH > CO\cdot NH_2$$

On the other hand, according to the hypothesis of permanent electron strain, the *m*-directive action should increase with increasing total dipole moment of the group, and this will depend on the disparity in the nuclear attractions exerted on the electrons held in common by two nuclei (Parts XIV and XV). The theoretical sequence is $C\cdot F > C\cdot O > C\cdot N > C\cdot C$; and, on the probable assumption that chlorine will resemble fluorine rather than oxygen, the order of the composite groups should be

$$\xleftarrow{\text{increasing } m\text{-directive power}}$$
$$\cdot CO\cdot Cl > \cdot CO\cdot OH > \cdot CO\cdot NH_2 > \cdot CO\cdot CH_3$$

Found (% *meta*-; temp. − 10° to − 15°):

(90%) (82%) (69%) (55%)

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* In processes where the mechanism depends upon formal conjugation, such as the activation of the three-carbon system, this is actually the order of the groups (compare Ingold, Shoppee, and Thorpe, J., 1926, 1482).

The numbers in the lower line * represent our results, the last figure being due to Camps, and it will be seen that they give support to the assumptions on the basis of which this sequence is deduced. We have not investigated benzoyl fluoride, but it would probably give a rather higher value than the chloride, and if it were substituted for the chloride in the above table the gaps between the successive members would be still more even than they are at present.

EXPERIMENTAL.

Nitration of Benzoyl Chloride.—The action of nitric acid on benzoyl chloride has been studied by Karslake and Huston (*J. Amer. Chem. Soc.*, 1909, **31**, 479), who used acetic anhydride as the solvent and observed complicated actions during which acetyl as well as nitro-groups entered the nucleus. Preliminary experiments having shown that complete hydrolysis accompanies (and probably precedes) nitration when nitric acid is used both as solvent and as nitrating agent, we operated in our final series with a mixture of nitrogen pentoxide and phosphorus pentoxide in carbon tetrachloride as solvent (compare Part I, J., 1925, **127**, 517). The temperatures ranged from −10° to −15°. Due care being taken in the preparation of the nitrogen pentoxide, it is possible under these conditions entirely to avoid hydrolysis, as was shown by evaporating the nitration solution in a slow stream of phosphorus pentoxide-dried air, which removes the excess of nitrogen pentoxide and any hydrogen chloride arising from hydrolysis, and then hydrolysing the residue with pure potassium carbonate, when the liberated chloride ion was found to be equivalent to the organic acids to within the limits of experimental error. If the nitrogen pentoxide used is contaminated with its double compound with nitric acid, a certain amount of hydrolysis may occur, but as this appears to make no difference whatever to the proportions of isomerides ultimately found, it is concluded that nitration by nitrogen pentoxide is rapid and that the hydrolysis is subsequent. The separation of the isomeric nitrobenzoic acids was carried out by the methods illustrated in previous papers of this series, which were again checked by application to artificial mixtures. It should, however, be mentioned that the proportion of *p*-isomeride formed in the present instance was smaller than the corresponding solubility correction (2%), so that we can only assign this value as a maximal limit. The values for the *m*-isomeride ranged from 90—91%, except one (Expt. 11; 89%) which is known to be low as a trace of *m*-acid was lost through the " creeping " of the ethereal solution.

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* It is unnecessary to discuss in detail all the disturbances which might affect the numerical data, because in every case there are reasons either of analogy or of theory for supposing that they would not affect the main result. Thus the figure for acetophenone may be slightly lower than corresponds with the true action of the acetyl group owing to the presence of a small amount of the enol form during nitration; but analogy with the nitration of the nitrobenzophenones (Staedel), where enolisation is impossible, shows that such a disturbance could not be serious; besides, nitration through the enol would lead to the *p*-derivative (Part II, J., 1925, **127**, 873), and actually scarcely any *p*-compound is formed. Some slight additional control might be obtained by the investigation of $\omega\omega'\omega''$-trialkylacetophenones, but we have little doubt that, owing to the polar disturbance of the alkyl groups (as previously illustrated for methyl and ethyl benzoates; J., 1926, 2466), these ketones would give lower, and not higher, meta-values than acetophenone itself. The possible small effects of imidolisation and hydrion addition act in opposite directions as regards the action of the carboxylamide group, and the ionisation of the benzoic acid in the nitric acid solvent would tend to lower the percentage of *m*-isomeride formed (this vol., p. 817, footnote). Even in water, however, the ionisation at a corresponding concentration would only be 0·2%, and it is clear both from an extrapolation of the figures for the benzoic esters (Holleman) and from our experiments on the nitration of benzoic acid in a non-ionising medium ($N_2O_5+CCl_4$) that the disturbance arising from electrolytic dissociation is negligible in comparison with the differences shown in the table above.

(Expt. 3.) Conditions: benzoyl chloride, 2·545 g.; nitrogen pentoxide, 10 g.; carbon tetrachloride, 50 g. containing phosphorus pentoxide in suspension; temperature, − 10°; time allowed for nitration, 2 hours. Results: benzoic acid, by sublimation, nil; *p*-nitrobenzoic acid, less than 2·1%; *m*-nitrobenzoic acid, 90·2%.

The mean (excluding Expt. 11) was 90·3% meta-, the mean temperature being −12·5°.

Nitration of Benzoic Acid.—These experiments need not be described in view of Holleman's previous investigation, and it suffices to state that our value for the proportion of *m*-isomeride formed by nitration at 0° by 10 parts by weight of nitric acid ($d^{16°}$ 1·505) is 80·0%, closely agreeing with Holleman's figure, 80·3%, for the same temperature. The value 81·7%, given in the introduction as 82%, is corrected to correspond with − 12·5° (the approximate mean temperature of the other nitrations) by means of Holleman's correction factor.*

As shown above (p. 839, footnote), the value 82% may be slightly lower than corresponds with the true action of the un-ionised carboxyl group, but the other value, namely 85·7%, which we have obtained by nitrating benzoic acid with nitrogen and phosphorus pentoxides in carbon tetrachloride under the conditions used for benzoyl chloride is almost certainly too high, since part of the material will doubtless have been nitrated as benzoic anhydride, which would be expected to give a definitely higher value than the un-ionised acid.

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* In a preliminary experiment on the nitration of benzoyl chloride by excess of fuming nitric acid at +15°, the value 78·6% was obtained for the proportion of *m*-isomeride. This experiment was done before it was realised that hydrolysis precedes nitration under these conditions, but it is now evident that the value agrees with Holleman's figure for the *nitration of benzoic acid* corrected to that temperature (78·3%), and with our own value similarly corrected (78·0%).

Nitration of Benzamide.—Benzamide was nitrated with excess of fuming nitric acid in the usual way and any nitrobenzoic acids formed by hydrolysis were separated from the neutral amides by means of ether and potassium carbonate. The hydrolysis accompanying nitration was usually of the order of 10%, and the degree of mononitration 97—100%. After analysis, the amides were hydrolysed by boiling for 16 hours with 8% potassium hydroxide solution, preliminary experiments with *m*-nitrobenzamide having shown that hydrolysis is complete and quantitative under these conditions. The nitrobenzoic acids were then separated as usual, any benzoic acid arising from incomplete nitration being previously eliminated by sublimation below 100°. Since it is not known whether the hydrolysis which occurs during nitration is antecedent or subsequent to the entrance of the nitro-group, the acid by-product was also separated into its component isomerides in order to see how each of these two alternative hypotheses would affect the result: actually it makes very little difference which view is adopted. On either hypothesis, the individual values for the proportion of *m*-nitrobenzamide formed all lay between 69 and 70%. The proportions of *p*-derivative being always less than the corresponding solubility correction, we are only able to quote 3% as a maximal limit.

(Expt. 44.) Conditions: benzamide, 2·00 g.; nitric acid ($d^{16°}$ 1·505), 30 g.; temperature, − 15°; time allowed for nitration, 6 hours. Results: hydrolysis, 10%; benzoic acid, nil; *p*-nitrobenzoic acid, less than 3%; *m*-nitrobenzoic acid, 69·6%. This is the proportion of *m*-nitrobenzamide formed if the 10% of hydrolysis entirely precedes nitration. The acid by-product contained 66% of *m*-isomeride, so that if the hydrolysis is wholly subsequent to nitration, the proportion of *m*-nitrobenzamide *formed* would be 69·2%. The mean value 69·4% is regarded as the most trustworthy.

The final mean is the same figure, *viz.*, 69·4% meta-. This, and the other mean figures, are rounded in the table given in the introduction, since it is doubtful if much significance attaches to the decimals.

THE UNIVERSITY, LEEDS.

[*Received, December* 21*st*, 1926.]

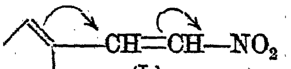
CXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XVII. The Directive Action of the Groups* $\cdot CH_2\cdot CH_2\cdot NO_2$, $\cdot CH{:}CH\cdot NO_2$ *and* $\cdot C(NO_2){:}CHR$ *in Aromatic Substitution.*

By John William Baker and Ian Stuart Wilson.

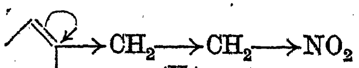
In preceding parts of this series (Goss, Ingold, and Wilson, J., 1926, 2440; Baker and Ingold, *ibid.*, p. 2462; this vol., p. 261) it is shown that positive poles and the positive ends of dipoles constitute strongly *m*-orienting influences, the effectiveness of which decreases with the intercalation of successive saturated carbon atoms between the charged atom and the nucleus (Goss, Hanhart, and Ingold, this vol., p. 250).

It has been generally assumed that the propagation of electronic disturbances originating in a polar group takes place much more readily in unsaturated carbon chains with conjugated double linkings than in fully saturated carbon chains of similar length, and there is little doubt that this is so in reactions which involve a complete co-valency change such as occurs in triad tautomerism and in the Michael and aldol reactions (Ingold, Shoppee, and Thorpe, J., 1926, 1482; Cooper, Ingold, and Ingold, *ibid.*, p. 1868).

On the other hand, the same view would also be implicit in mechanisms of *m*-substitution in which the conjugation between the nuclear and the side-chain double linking played a fundamental rôle (compare Part XVI), and on the basis of such mechanisms it is to be expected that the transmission of a *m*-orienting influence would be facilitated by the presence of an unbroken conjugated system extending from the polar group throughout the nucleus; thus, on this view, the ω-nitrovinyl group (I) should be more strongly *m*-orienting than the ω-nitroethyl group (II), and so on:



(I.)



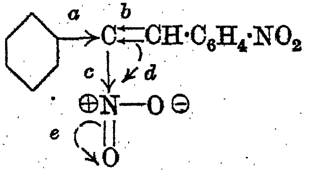
(II.)

Nevertheless, it may be thought doubtful whether such radical electronic disturbances occur even momentarily in the reactions considered, and whether the conjugation referred to is essential to the process of orientation; a preferable view seems to be (Baker and Ingold, Part XV, this vol., p. 833) that a strain or small shift of average position of the electrons is propagated from the polar group, and that it is the degree of inequality in which the electrons are shared at the junction with the aromatic nucleus which determines the *m*-orienting action of the group. If this be so, then, although the arrangement and mobility of the electrons in a non-polar double linking are still matters of speculation, the ethylenic bond undoubtedly represents a high degree of unsaturation which must arise from an adjustable electric field at this point, and therefore it is conceivable that the effect due to a positive charge, such as that of the nitro-group in ω-nitrostyrene, will be neutralised during passage through this field, and never reach the nucleus; the true orienting group will then be the α-carbon atom, and the behaviour of the compound to substituting agents should resemble that of toluene (compare Priebs, *Annalen*, 1886, **235**, 347). Toluene, on nitration in nitric acid, gives 3% of *m*-derivative. On the other hand, the hypothesis (Baker and Ingold, Part XI, this vol., p. 261) of the equivalence between the dipoles of a nitro-group and a primary ammonium salt group (Moore's constitution) requires that β-phenylnitroethane should yield the same proportion of *m*-nitro-derivative as does β-phenylethylamine. β-Phenylethylamine, on nitration, gives 12% of *m*-derivative (Goss, Hanhart, and Ingold, Part X, *loc. cit.*). Hence β-phenylnitroethane should, on this theory, yield definitely more than the unsaturated analogue. Experimental evidence, therefore, should enable a decision to be made between the two suggested mechanisms.

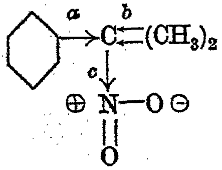
We find that ω-nitrostyrene, on nitration, yields 2% of the *m*-nitro-derivative, whilst β-phenylnitroethane under similar conditions gives 13%.

There is another possible explanation of this result, namely, that the vinyl double bond itself acts as a powerful electron source towards the nucleus, and thus dominates the electron-attraction of the nitro-group. To test this possibility, we have investigated the nitration of an α-nitrovinylbenzene, *viz.*, *p*-nitrobenzylidenephenylnitromethane (III), in which the double bond is similarly situated with respect to the nucleus but is not in the path of transmission from the nitro-group. In this case, we find more than 20% of *m*-substitution, from which it is clear that the vinyl group, as such, has not a powerful *op*-orienting influence. Indeed, it seems remarkable that the double bond does not compete more effectively with the phenyl group in satisfying the electron-demand of the

(III.)



(meta, 21%)



(IV.)

(meta, 29%)

nitro-group, until it is remembered that each change (*d*) will be accompanied by a change (*e*) on which it is dependent, and that the two together do not alter the charge on the nitrogen atom. All that competes with the *m*-orienting shift (*a*) in satisfying the electron demand (*c*) of the positive pole is the strain represented by (*b*) (inequality of sharing) and it is therefore not surprising that the effect of a group :CHR in modifying the directive action of a nitromethyl side-chain is not much greater than that of the *gem*-dimethyl group (IV) (Baker and Ingold, Parts IX and XI, *loc. cit.*).

EXPERIMENTAL.

A. *Preparation of Materials.*—ω-*Nitrostyrene* was prepared by Thiele and Haeckel's method (*Annalen*, 1902, **325**, 7).

α-*Nitro*-β-*phenylethane* was prepared in accordance with the scheme : $CH_2Ph{\cdot}CH_2{\cdot}OH \xrightarrow{PBr_5} CH_2Ph{\cdot}CH_2Br \xrightarrow{AgNO_2} CH_2Ph{\cdot}CH_2{\cdot}NO_2$. Phosphorus pentabromide in slight excess was added in small, successive portions to β-phenylethyl alcohol, cooled in a freezing mixture. The reaction mixture was finally heated for 0·25 hour on the steam-bath. The product, after cooling, was poured on ice and water, the bromide extracted with ether, and the ethereal solution washed with water and with sodium carbonate solution. The residue from the dried ethereal extract had b. p. 99—103°/14 mm. (compare Grignard, *Compt. rend.*, 1904, **138**, 1049).

A mixture of the bromide and freshly prepared, dry silver nitrite in equal molecular quantities was left in the dark, with frequent shaking, for 1 week. It was then heated at 50—60° for 2 hours, the nitro-compound extracted with ether, the residue from the ether dissolved in dilute sodium hydroxide solution, and the insoluble, unchanged bromide extracted with ether. The nitro-compound was precipitated from the alkaline solution with carbon dioxide, extracted with ether, and the residue from the dried, ethereal extract distilled. α-*Nitro*-β-*phenylethane* has b. p. 125—135°/1 mm. (Found: * C, 61·4; H, 5·8; N, 10·1. $C_8H_9O_2N$ requires C, 63·5; H, 6·0; N, 9·3%). The yield was very small.

p-*Nitrobenzylidenephenylnitromethane.* To phenylnitromethane (5·6 g.) and *p*-nitrobenzaldehyde (6·0 g.), 1 c.c. of 33% aqueous methylamine was added, and the mixture was warmed on the steam-bath (with addition of a few drops of alcohol if necessary) until solution was complete. After remaining for 24 hours at the ordinary temperature, the now almost solid product was filtered off, washed with a little alcohol, and recrystallised from ethyl acetate containing a little ligroin (b. p. 80—100°), being thus obtained in fine, yellow needles, m. p. 155° (Found: C, 62·0; H, 3·9. $C_{14}H_{10}O_4N_2$ requires C, 62·2; H, 3·7%).

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* Methane produced during the combustion accounts for the low result for carbon. The gas obtained in the nitrogen determination (Dumas) contained nitrogen 84·1%, combustible gas (chiefly methane) 15·9%.

B. *Nitration Conditions and General Procedure.*—Nitration was carried out in every case at —15° to —10°, the compound being added slowly to 8—10 volumes of nitric acid (*d* 1·49), mechanically stirred. The product was isolated in the usual manner, the details varying slightly in individual cases. The proportions of the isomerides present were determined by oxidation with 2% potassium permanganate, either before or after separation of most of the *p*-isomeride in the pure state, and determination of the mixed nitrobenzoic acids produced, by Baker and Ingold's method (*loc. cit.*) or the titration method (Baker, this vol., p. 565).

C. *Details relating to Individual Cases.*—*ω-Nitrostyrene* was nitrated by Priebs (*loc. cit.*), who isolated the *o*- and *p*-derivatives, but could find no *m*-isomeride.

(*Expt.* 11.) The nitrostyrene (10 g.) was added in small successive portions to 75 c.c. of nitric acid (*d* 1·49) at —15° during 2 hours, and after a further 3 hours the partly crystalline product was poured on crushed ice and the precipitated nitro-compounds were filtered off, washed, and dried over phosphorus pentoxide in a vacuum (91·5%). A further 3·8% of nitro-compounds was obtained from the dried ethereal extract of the mother-liquor, from which any acid fraction had been removed (total yield, 95·3%) (Found: C, 49·4; H, 3·4. Calc.: C, 49·5; H, 3·1%).

A portion (3·00 g.) of the total nitration product on oxidation gave nitrobenzoic acids in 91% yield (*M*, by titration, 166·7). These, on separation by the chloroform–barium salt method, yielded 1·96 g. of *p*-nitrobenzoic acid, m. p. 228—230°, mixed m. p. 234—235°, which, with the solubility correction (0·05 g.), corresponds to 67% of this isomeride in the mixture. On conversion of the dissolved acids into their barium salts and concentration of the solution to 30 c.c., no crystallisation ensued. Hence the meta-content must be less than 0·06 g., *i.e.*, less than 2% of the whole mixture. On acidification and extraction with ether, the solution of the barium salts yielded 0·89 g. of *o*-nitrobenzoic acid, m. p. 115—130° (corresponding to 30% of the whole), which, after two crystallisations from chloroform, melted alone at 137°, at 145° when mixed with *o*-nitrobenzoic acid, and at 108—120° when mixed with *m*-nitrobenzoic acid. The composition of the nitration product is therefore *p*- 67%, *m*- <2%, *o*- (by difference) 31% (30% being actually isolated). The proportion of meta-isomeride in the mixture of nitrobenzoic acids obtained by an independent oxidation (yield

81·9%) of this nitration product, determined by the titration method, was 1·9%.

(*Expt.* 12.) The main portion of the *p*-isomeride was isolated from the nitration product (yield 99%) (Found: C, 49·5; H, 3·4%) before oxidation. The nitration product (5·105 g.) on extraction with 100 c.c. of boiling, absolute alcohol left a residue (α) (2·274 g.); the extract deposited 1·449 g. of crystals (β). The mother-liquor was evaporated to dryness (γ) on the steam-bath. The fraction α had m. p. 200° (softening at 190°) and was pure ω*p*-dinitrostyrene. On oxidation, the fraction β gave nitrobenzoic acids in 94% yield (*M*, 167·5), which on separation gave *p*-, m. p. 228°, 0·501 g. (65%); no *m*-; and *o*-, (by difference) 35%, of which 31% was actually isolated, m. p. (after crystallisation from chloroform) 144—145°, mixed m. p. 147°. Fraction γ, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 170), which on separation gave *p*-, m. p. 210—220°, 17·9%; *m*-, m. p. 110—114°, mixed m. p. with *m*- 128—131°, mixed m. p. with *o*- 98—120°, 10·1%; *o*- (by difference) 72%, of which 63% was isolated, m. p. 141°, mixed m. p. 142—145°. The composition of the nitration product is therefore: *p*- = 44·3% (α) + 18·4% (β) + 4·8% (γ) = 67·5%; *m*- = 2·7% (γ); *o*- (by difference) = 29·8%.

α-Nitro-β-phenylethane. Since only a very small quantity of this substance was available, owing to the difficulty of preparation, the result obtained can only be regarded as approximate. The quantity of *m*-isomeride found is, however, in agreement with that obtained on nitration of the corresponding ammonium salt $CH_2Ph{\cdot}CH_2{\cdot}\overset{+}{N}H_3{\cdot}\overset{-}{X}$ (compare p. 843).

(*Expt.* 21.) The nitro-compound (1·069 g.) was added to 15 c.c. of nitric acid (*d* 1·49) at —15° to —10° during 50 minutes, and after ½ hour the temperature was allowed to rise to —5°, a slight evolution of brown fumes then being observed. The product was poured on crushed ice, and the solution obtained was neutralised partly with 10% aqueous sodium hydroxide and finally with precipitated chalk, and extracted with ether. The yield of neutral nitration product was 78·5% (Found: C, 49·8; H, 4·0. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·2%); acid products amounted to 10·8%. The neutral portion, on oxidation, gave nitrobenzoic acids in 70% yield (*M*, 164) (benzoic acid, by sublimation, 10·5%, which was deducted in calculating the percentages of isomerides present), of which 29·4% consisted of *p*-nitrobenzoic acid, m. p. 224—228°, which crystallised, the remainder being extracted with ether. Separation of a representative sample of the extracted portion in the usual manner showed it to consist of *p*-, m. p. 210—215°, mixed m. p. 220—224°, 32·5%; and *m*-, m. p. 123—125°, mixed m. p. 135—137°, 18·9%, whence the composition of the nitration mixture was *p*-, 29·4% + (32·5% of 70·5%) = 52·3%; *m*-, (18·9% of 70·5%) = 13·3%; *o*- (by difference), 34·4%.

p-*Nitrobenzylidenephenylnitromethane.* (*Expt.* 31.) In this, a preliminary experiment, the nitromethane (0·832 g.) was added to 10 c.c. of nitric acid (*d* 1·49) at —20° to —15° during 0·75 hour, the product was left in the freezing mixture for 1·3 hours and then poured on crushed ice, and the precipitated solid (yield 82%) was filtered off, washed, and dried in a vacuum over phosphorus pentoxide (Found: C, 52·9; H, 3·3. $C_{14}H_9O_6N_3$ requires C, 53·3; H, 2·9%). On oxidation, the nitro-compound gave nitrobenzoic acids in 90% yield, a large proportion of the *p*-isomeride being allowed to crystallise before extraction of the mother-liquor with ether. Separation by the chloroform–barium salt method gave, after deduction of the *p*-nitrobenzoic acid produced by oxidation of the *p*-nitrobenzylidene portion of the molecule, *p*-, m. p. 235°, 49%; *m*-, m. p. 125°, mixed m. p. 137—138°, 19·5%; *o*- (by difference), 31·5%.

(*Expt.* 33.) The nitromethane (2·02 g.) gave, under the same conditions as before, 2·306 g. of precipitated nitro-compound (Found: C, 52·6; H, 3·1%) and 0·032 g. extracted with ether (total yield 96%), of which 1·861 g. on oxidation gave 1·081 g. of *p*-isomeride, m. p. 228—232°, mixed m. p. 235°, and 0·540 g. of extracted acids (*M*, by titration, 170) (total yield 83%). On separation, 0·473 g. of the extracted acids gave 0·079 g. of *m*-acid (crystallised), m. p. 131—133°, mixed m. p. 140—141°, and 0·074 g. (extracted), m. p. 124°, mixed m. p. 138° (solubility correction, 0·0054 g.), and 0·077 g. of *p*-nitrobenzoic acid, m. p. 230—232° (solubility correction, 0·007 g.). Hence the composition of the whole of the nitrobenzoic acids obtained (1·620 g.) was *p*-, 1·080 + 0·540/0·473 of (0·077 + 0·007) = 1·175 g.; *m*-, 0·540/0·473 × 0·153 = 0·175 g. Of this 50%, the total yield, 0·810 g. is *p*-nitrobenzoic acid obtained from the oxidation of the *p*-nitrobenzylidene group, so that the 0·810 g. of mixed nitrobenzoic acids obtained by oxidation of the nitrated benzene ring contained *p*-, 0·365 g., and *m*-, 0·175 g., whence the composition is *p*-, 45·1%; *m*-, 21·6%; *o*- (by difference), 33·3%.

(*Expt.* 34.) Under the same conditions as before and by analogous methods of separation, 2·20 g. of the nitromethane yielded 2·542 g. (96%) of neutral nitration product (Found: C, 53·4; H, 2·7%), which, on oxidation, gave nitrobenzoic acids (95% yield) (*M*, 166·8; benzoic acid, by sublimation, 1·6%). Separation as before showed that the composition of the nitrobenzoic acids representing the proportions of isomerides formed by nitration was *p*-, m. p. 233°

either alone or mixed with a pure specimen, 49·7%; *m*-, m. p. 135°, mixed m. p. 141°, 20·9%; *o*- (by difference), 29·4%.

The results obtained are summarised below.

	Percentage of isomerides.					
	By separation.			By titration.	Mean %.	
Substance nitrated.	*o*.	*m*.	*p*.	*m*.	*m*.	*p*.
CHPh:CH·NO_2	31	<2	67	1·9	2	67
	29·8	2·7	67·5			
CH_2Ph·CH_2·NO_2	34·4	13·3	52·3	—	13	52
CPh(NO_2):CH·C_6H_4·NO_2	31·5	19·5	49·0	—	21	48
	33·3	21·6	45·1			
	29·4	20·9	47·9			

We desire to thank Professor C. K. Ingold, F.R.S., for his kindly and helpful interest in this investigation, and the Royal Society for defraying part of the expense incurred.

THE UNIVERSITY, LEEDS. [*Received, January 15th*, 1927.]

CXXIII.—*The Determination of Carbonyl in Aldehydes and Ketones.*

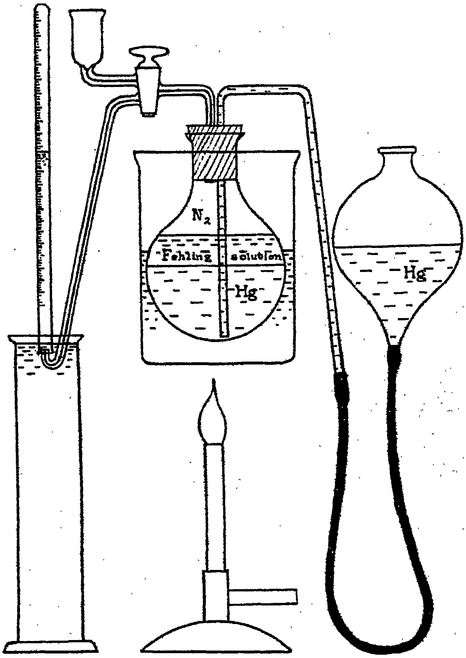
By GEORGE WILLIAM ELLIS.

THE present method is a modification of one described by Strache (*Monatsh.*, 1891, **12**, 514; 1892, **13**, 299). It depends essentially upon the formation of phenylhydrazones and estimation of the excess of phenylhydrazine by measuring the nitrogen evolved by the action of Fehling's solution ($C_6H_5\cdot NH\cdot NH_2 + O = C_6H_6 + N_2 + H_2O$), a control being carried out upon phenylhydrazine alone. Since the hydrazones do not evolve nitrogen, and since few compounds are likely to interfere with the reaction, the method is of wider application than any other that has been proposed.

Strache used steam to drive out the air from his apparatus and, subsequently, to transfer the evolved nitrogen to the eudiometer, where it was measured saturated with water and benzene vapour. Watson Smith (*Chem. News*, 1906, **93**, 83) substituted carbon dioxide for steam and protected the Fehling's solution by means of a layer of paraffin. Also, to avoid the correction for benzene vapour, the small quantity evolved was nitrated and so absorbed. His apparatus was therefore more elaborate than that of Strache. Both workers recorded satisfactory results, but in the author's experience, both methods are unnecessarily tedious and often untrustworthy. Watson Smith appears to have attributed this to Strache's use of steam, which may cause an evolution of air from the generator or from the water under the eudiometer; but carbon dioxide is required in such quantities as to heat the alkaline solution under the eudiometer and thus cause a similar error. Since, however, nitrogen is soluble in water at 100° to the extent of nearly 1% by vol. (Winkler), it will be appreciated that the delay in the cessation of the appearance of nitrogen in the eudiometer is almost entirely due to the solubility of this gas in the solutions employed in the reaction mixture. Strache recommended the use of 200 c.c. of Fehling's solution and about 50 c.c. of the phenylhydrazine solution. Further, the experiments were adjusted so as to yield about 20 c.c. of gas both in the actual estimation and in the control. Hence about 15% of the nitrogen may be retained in solution. This is slowly evolved by the passage of steam through the solutions in Strache's method, but it must be indefinitely retained in the paraffin-protected solutions employed by Watson Smith.

The method now described almost entirely obviates the above disadvantages, and utilises the well-known fact that dissolved gases can only be rapidly removed from their solutions by vigorous ebullition under reduced pressure. Further, it is not necessary to arrange for the production of the same volume of nitrogen in the two measurements of each estimation, and thus another possible source of error, due to manipulation of aliquot parts, is avoided.

FIG. 1.



EXPERIMENTAL.

At the bottom of a strong, short-necked, round-bottomed flask of about 300 c.c. capacity (Fig. 1) are placed about 250 c.c. of mercury, connected with a smaller quantity in a reservoir by means of a glass tube of about 3 mm. bore and rubber tubing. Above the mercury in the flask are placed about 50 c.c. of Fehling's solution. The two-way stopcock connects the upper part of the flask either with a cup of 5—10 c.c. capacity or with the eudiometer, both connexions being of capillary tubing. The flask is almost completely surrounded by a beaker, but only a little boiling water is contained in the latter.

The Fehling's solution must first be freed from dissolved gases. The water in the beaker is kept rapidly boiling, the stopcock is closed, and the mercury reservoir is lowered as far as possible so as to reduce the pressure in the flask. When most of the mercury in the flask has been forced into the reservoir by the vapour formed, the rubber tubing is pinched by a clip and a fine jet of cold water is directed upon the upper surface of the flask. The reduced pressure in the flask causes a vigorous ebullition, and by maintaining as great a difference of temperature as possible between the upper and lower parts of the flask, the greater part of the dissolved gases is removed from solution. After about 5 minutes' constant attention to these conditions, the reservoir is raised, the clip is removed, and the gases are forced out of the apparatus. The process is repeated until only a small break, or a slight froth, passes through the capillary tubing. This operation takes about 15 minutes if only 50 c.c. of Fehling's solution are used. A similar treatment is applied at the end of the actual estimations of nitrogen.

A pipette of about 2 c.c. capacity was constructed from tubing of 5—6 mm. bore by drawing it to a fine orifice at one end and melting to a fine, short constriction in the middle. When this pipette is filled with fluid just above the constriction and held with the outlet touching the wall of a container, the liquid automatically stops at the constriction. The quantity so retained, after being blown and washed out, varies to only a fraction of a mg.

About 0·43 g. of phenylhydrazine hydrochloride, with a similar quantity of anhydrous sodium acetate, was dissolved in 3 measures of water from the pipette, and the solution filtered. Of this, 2 measures were conveyed to separate tubes, the third being employed for rinsing the pipette. In one tube, having a thickened bottom, was broken a small bulb containing 0·0619 g. of salicylaldehyde. Both tubes were placed in a water-bath for a few minutes.

The contents of the tube which held the reagent only were placed in the cup of the apparatus and drawn into the flask by careful lowering of the reservoir. The tube and cup were washed several times, and the washings drawn in, the whole of the phenylhydrazine being thus brought to the top of the Fehling's solution. The reservoir was then lowered until vapour formed at the top of the flask, thereby causing a mixing of the reagents and an evolution of nitrogen and benzene vapour. It may be noted here that an alcoholic solution of the hydrazine base may be employed and that some care must be exercised at this stage, for an injudicious lowering of the reservoir may produce so much vapour as to force the Fehling's solution out of the flask. In the actual experiment described, the greater part of the mercury was allowed to pass into the reservoir, and the water in the beaker was kept boiling for 3 or 4 minutes, after which most of the nitrogen was transferred to the eudiometer. The remainder of the nitrogen, which was chiefly in solution in the reaction mixture, was removed as described above for the preliminary operation; 20·0 c.c. at 16° and 773·7 mm. were obtained, measured saturated with aqueous and benzene vapours as recommended by Strache.

The excess of phenylhydrazine remaining in the other tube was then estimated. It was necessary to filter off the hydrazone so as to prevent clogging of the capillary; this was effected by means of a small drawn-out tube, plugged with cotton wool and leading into another tube placed in a vacuum filtering-flask. It was thus possible to filter and wash the hydrazone so that the total bulk of liquid was no more than that used in the first estimation. The excess of the reagent, under exactly the same conditions, yielded 9·3 c.c. (Found: CO, 22·2. Calc.: CO, 22·9%).

The results of various estimations by the new method are given below. For those in which more than 0·1 g. of material was taken, 200 c.c. of Fehling's solution were employed, as used by Strache; but the author's method of using smaller quantities was found to be more rapid and even more accurate. The substances taken were carefully purified for the purpose, but their degree of purity was not ascertained.

Results.—Salicylaldehyde; found: CO, 22·2, 24·8, 23·2; calc., 22·9%. Acetone; found: CO, 47·3; calc., 48·2%. Phenylhydrazine; found, 102, 100·1%. Phenylhydrazine hydrochloride; found, 99, 102%.

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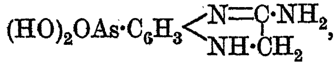
[*Received, February 22nd,* 1927.]

CXXIV.—*Heterocyclic Compounds containing Arsenic. Part I. The Action of Chloroacetamide on* 3:4-*Diaminophenylarsinic Acid.*

By Arthur James Ewins, George Newbery, and Ralph William Ewart Stickings.

In the course of investigations in connexion with the chemotherapy of organic arsenical derivatives, our attention was recently directed to a communication by Lewis and Bent (*J. Amer. Chem. Soc.*, 1926, 48, 949) in which the action of chloroacetamide on 3:4-diaminophenylarsinic acid (I) is discussed. These authors consider that under their conditions of experiment chloroacetamide reacts preferentially with one amino-group with the production of 3-aminophenylarsinic acid 4-glycineamide (V). They state also that, if the reaction be not carefully controlled, ring closure takes place with elimination of water and the formation of a quinoxaline derivative,



$(HO)_2OAs\cdot C_6H_3<\begin{matrix}N{=}C\cdot NH_2\\ NH\cdot CH_2\end{matrix}$,

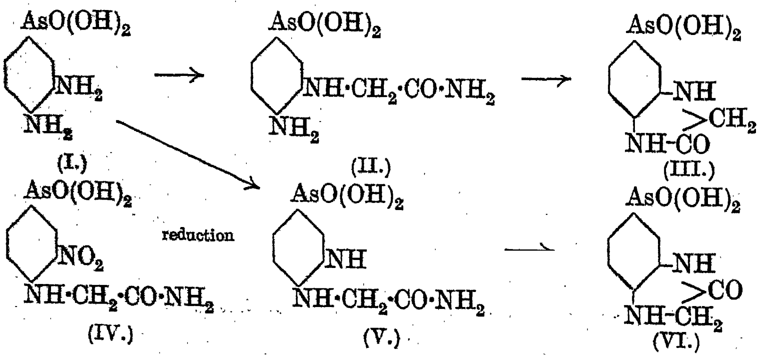
the reaction being analogous to the formation of a phenylquinoxaline from ω-bromoacetophenone and *o*-phenylenediamine (Fischer and Romer, *Ber.*, 1908, **41**, 2350). The reaction is suggested as a new method of preparing quinoxalines containing an amino-group.

The production of 3-aminophenylarsinic acid 4-glycineamide is of interest, as this compound is a derivative of tryparsamide, phenylarsinic acid 4-glycineamide, which is a product of considerable therapeutic value.

One of us (R. W. E. S.) had already attempted the preparation of the amino-derivative of tryparsamide by reduction of the corresponding nitro-compound (IV), but the experiments invariably resulted in the production of what we were able to show was 3-*hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid* (VI).

We were therefore led to repeat the work of Lewis and Bent (*loc. cit.*) and we were unable to confirm their conclusions. Following the directions given on p. 955 of their paper, we obtained a product which we were able to show consisted of a mixture of two isomeric hydroxydihydroquinoxalinearsinic acids, one of which was identical with that produced by the reduction of 3-nitrophenylarsinic acid 4-glycineamide.

It seems obvious, therefore, that chloroacetamide reacts with both amino-groups of 3 : 4-diaminophenylarsinic acid, ring closure taking place in each case with elimination of ammonia and formation of a quinoxaline derivative according to the following scheme, the intermediate amino-derivatives (II and V) being unstable.



The formation of these quinoxalines has been confirmed by analysis. Lewis and Bent apparently only determined the percentage of arsenic in their product. Determination of nitrogen would have undoubtedly shown them the true nature of the compound produced.

The constitution of 3-hydroxy-1 : 4-dihydroquinoxalinearsinic acid (VI) is established by its identity with the product obtained by reduction of 3-nitrophenylarsinic acid 4-glycineamide (IV). It is therefore highly probable that (III) has the constitution denoted, and experiments are in progress to establish this by synthetic methods also.

EXPERIMENTAL.

Action of Chloroacetamide on 3 : 4-*Diaminophenylarsinic Acid.*—Following the procedure outlined by Lewis and Bent (*loc. cit.*), 25 g. of 3 : 4-diaminophenylarsinic acid were dissolved in a solution of 4·1 g. of sodium hydroxide in 105 c.c. of water, 19·4 g. of chloroacetamide were added, and the mixture was boiled under reflux for 45 minutes. Concentrated hydrochloric acid (7·8 c.c.) was added to the cooled solution. A crystalline solid readily separdate which was seen under the microscope to consist of a mixture of long, fine needles and tetrahedra. The product was in part somewhat readily soluble in hot water, completely soluble in dilute alkali solution, and insoluble in dilute mineral acids. Treatment with caustic soda solution produced only a trace of ammonia. The crude product was purified by reprecipitation from dilute sodium carbonate solution after treatment with charcoal (yield, 15 g.) (Found: As, 27·5; N, 10·5. $C_8H_9O_4N_2As$ requires As, 27·6; N, 10·3%).

Separation of the Isomeric Quinoxalines.—The product (12 g.) was boiled with successive quantities (50, 25, 25, 25 c.c.) of water, the hot extracts were combined, and the crystalline product obtained on cooling was repeatedly crystallised from water, being finally obtained in long, nearly white, prismatic needles, which did not decompose at 260°. Analysis indicated it to be 3-*hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid* (VI) (Found: As, 27·4; N, 10·35%).

A *monobenzoyl* derivative was obtained by the Schotten–Baumann method. It crystallised from 50% alcohol, in which it was readily soluble, in lustrous, hexagonal plates, which did not decompose below 290° (Found: As, 19·85; N, 7·45. $C_{15}H_{13}O_5N_2As$ requires As, 20·0; N, 7·4%).

3-Hydroxy-1 : 4-dihydroquinoxaline-6-arsinic acid was readily obtained again on boiling the monobenzoyl derivative with 5% sodium hydroxide solution for 15 minutes.

2-*Hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid* (III) was obtained by purification of the less soluble fraction (about 6·8 g.) left after extraction of the original mixture with hot water. Owing to the general insolubility of the compound in neutral solvents, purification was effected by means of the sodium salt. The acid was dissolved in just sufficient sodium carbonate solution to produce a neutral or faintly alkaline solution. To the hot filtered solution alcohol was added gradually until crystallisation of the sodium salt commenced. On standing, a semi-solid crystalline mass of needles was obtained. The crystals were filtered off, washed with a little alcohol, and dissolved in hot water, and the hot solution was made just acid to Congo-red. On standing, the *acid* separated in diamond-shaped plates, m. p. 258° (decomp.) (Found: As, 27·7; N, 10·4%).

A *monobenzoyl* derivative was obtained in the usual way. The alkaline reaction product was made just acid to Congo-red with dilute hydrochloric acid, and the precipitated benzoic acid removed in ether. The aqueous solution slowly deposited the *benzoyl* derivative, which crystallised from water in stout, hexagonal plates, m. p. 251—252° (Found: As, 20·1; N, 7·8%).

Nitration of Phenylarsinic Acid 4-*Glycineamide*.—A solution of 220 g. of the sodium salt of phenylarsinic acid 4-glycineamide in 800 c.c. of concentrated sulphuric acid was cooled to 0° and slowly treated with a mixture of 46 c.c. of nitric acid (*d* 1·42) and 46 c.c. of concentrated sulphuric acid, the temperature being maintained below 5°. After being kept for 30 minutes, the reaction mixture was poured on 1 kg. of ice, 4 litres of water were added, and the whole was stirred; crystallisation then started. After cooling to 0°, the crystals were filtered off, washed free from mineral acid, and dried. The product was an intensely yellow, crystalline substance (yield, 155 g.) soluble in alkalis to a dark red solution (Found: As, 23·4; N, 13·2. $C_8H_{10}O_6N_3As$ requires As, 23·5; N, 13·2%).

Reduction of 3-*Nitrophenylarsinic Acid* 4-*Glycineamide with Ferrous Hydroxide. Production of* 3-*Hydroxy*-1 : 4-*dihydroquinoxaline*-6-*arsinic Acid*.—3-Nitrophenylarsinic acid 4-glycineamide (100 g.) was dissolved in 800 c.c. of saturated sodium carbonate solution, and added to a cooled precipitate of alkaline ferrous hydroxide produced by pouring a solution of 300 g. of caustic soda in 400 c.c. of water into a cooled solution of 800 g. of ferrous sulphate in 800 c.c. of water. The temperature of the reduction was maintained at 30° for 1 hour, with occasional stirring, during which a strong smell of ammonia was noticed. The reaction mixture was then filtered, and the yellow filtrate was acidified to Congo-paper by addition of 50% sulphuric acid, crystallisation commencing immediately. After 10 minutes, the crystals were filtered off, washed, and purified by solution in dilute aqueous sodium carbonate and reprecipitation with excess of mineral acid. The product so obtained was a yellowish-white, crystalline substance, soluble in alkalis and insoluble in mineral acids. No ammonia was evolved on warming it with excess of caustic soda solution. It was moderately easily soluble in boiling water, from which it crystallised in long, prismatic needles which did not decompose below 260° (yield, 45 g.) (Found: As, 27·5; N, 10·4. Calc. for $C_8H_9O_4N_2As$: As, 27·5; N, 10·3%). This substance was identified with the compound (VI) by its crystalline form, solubility, and analysis and also by comparison of the monobenzoyl derivatives.

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Wandsworth, S.W. 18. [*Received, January* 21*st*, 1927.]

CXXV.—*The Properties of Malonic Anhydride (Carbon Suboxide)*, C_3O_2.

By Morris J. Edwards and John M. Williams.

A quantity of carbon suboxide has been prepared by the method of Diels and Meyerheim (*Ber.*, 1907, **40**, 359) with a view to the study of the kinetics of its process of polymerisation in the gaseous state. Also, since it was a comparatively simple matter to prepare the oxide in the pure state, the vapour pressure was measured over the range − 62° to 4°.

The oxide in the gaseous state proved to be very stable, even at room temperature, when dry and contained in a glass vessel the surface of which had not been previously contaminated with the polymerised product. On the other hand, it could not be stored over mercury for any length of time, or in the presence of moisture without polymerisation occurring. The dried gas is not appreciably affected by insolation with ultra-violet light.

The polymerisation occurs on the surface of the containing vessel, and from the measurement of the velocity of chemical change, the process is seen to be very complex.

Experimental.

The method of Diels and Meyerheim was adopted with slight modifications. Mixtures of 20 g. of pure malonic acid and 200 g. of powdered phosphorus pentoxide were placed in a 350 c.c. flask of hard glass and, after evacuation by means of a Langmuir pump heated by suddenly plunging the flask into an oil-bath at 140

160°. The gases liberated were withdrawn as rapidly as possible from the hot flask and cooled by passage through tubes immersed in a freezing mixture of ice and salt, and in liquid air. A mixture of acetic acid, carbon dioxide and carbon suboxide condensed in the tube immersed in liquid air. The temperature of the mixture was allowed to rise slowly and the bulk of the carbon dioxide evaporated into the air. When a temperature of 7° was reached, the gas was collected in a mercury reservoir; the first fraction was rejected, as it was contaminated with much carbon dioxide, and the second fraction was condensed as rapidly as possible in a 3 c.c. bulb immersed in liquid air. The liquid carbon suboxide was freed from carbon dioxide at −50° by connecting the bulb repeatedly with an evacuated space (10 c.c.) until the liquid gave a constant vapour pressure. The purity of the preparation was shown by the vapour density, which was 34·3.

Determinations of Vapour Pressure at Various Temperatures.—About 2 c.c. of carbon suboxide were condensed in a small bulb, to which was attached a mercury manometer by a glass-to-glass connexion. Since the suboxide slowly polymerises on the surface of mercury, the manometer was shut off by a tap except when measurements were being taken. Vapour-pressure determinations were made between −62° and 4°, in a bath of alcohol contained in a Dewar vessel as a thermostat. The alcohol was cooled by means of solid carbon dioxide. After every reading the bulb was placed in liquid air, and the vapour-pressure readings showed that no appreciable decomposition occurred throughout the experiments. In the table are given the readings of the manometer. Those at −62° are the successive values obtained during the removal of carbon dioxide.

Vapour Pressure Readings.

Temp.	−62°	−62°	−62°	−62°	−62°
Vap. press. (cm.)	5·80	3·55	2·85	2·45	2·30
Temp.	−62°	−62°	−52°	−44°	−39°
Vap. press. (cm.)	2·30	2·30	3·83	6·48	8·67
Temp.	−35°	−31°	−27°	−24°	−21°
Vap. press. (cm.)	10·97	13·61	16·69	19·34	22·37
Temp.	−16°	−11°	−6°	0°	+4°
Vap. press. (cm.)	28·47	35·97	44·62	57·52	67·32

From the vapour pressure curve, the boiling point at atmospheric pressure is 6·8°.

The heat of vaporisation was calculated from the above data by means of the expression $d \log p/dT = -Q/RT^2$, and the values for the range of temperature −62° to 4° are given below.

Values of Q for the Different Temperature Ranges.

Range ...	−62° to −52°	−52° to −44°	−44° to −39°	−39° to −35°
Q (Cal.) ...	4·74	6·62	6·16	6·57
Range ...	−35° to −31°	−31° to −27°	−27° to −24°	−24° to −21°
Q (Cal.) ...	6·18	6·03	6·02	6·06
Range ...	−21° to −16°	−16° to −11°	−11° to − 6°	− 6° to 0°
Q (Cal.) ...	6·22	6·27	6·00	6·14
Range ...	0° to 4°			
Q (Cal.) ...	5·93			

The mean value of Q between −31° and 4° is 6·08 Cal.

Velocity of Chemical Change.—Purified liquid carbon suboxide was vaporised into a glass bulb of 80 c.c. capacity. The bulb had been used previously in an experiment in which a red film of polymerised product had been deposited. This was removed by means of water and chromic acid. The polymerisation was accompanied by a decrease in pressure. The pressure was observed at constant volume and temperature (12°). The following readings were obtained for an initial gas pressure of 44·39 cm.

Time (hrs.)	0·25	0·75	1·75	2·75	4·75	6·75
Change of press. (cm.) ...	0·55	2·90	3·86	4·08	4·25	4·50

The values of the velocity coefficient, k, calculated from the above data, on the assumption that from 1 to 6 molecules may be taking part in the change, fall off with time. The reaction is probably a catalytic surface reaction. The fact that the speed of the reaction falls off with time may be explained by the fact that the vapour must diffuse through the layer of decomposed or polymerised product to the surface of the glass before it can undergo change.

Our thanks are due to Mr. W. E. Garner for his helpful advice and the interest which he took in the work.

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University College, London. [*Received, February 3rd*, 1927.]

CXXVI.—*The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. Part II.*

By Robert Winstanley Lunt and Ramavenkatasubbier Venkateswaran.

In the first communication of this series (J., 1925, **127**, 2052) an account was given of the decomposition of a fixed amount of carbon monoxide, enclosed in the annular space of a Siemens ozoniser, when subjected to ionisation by collision produced by alternating electric fields of frequency 250 cycles per sec. The decomposition was accompanied by the formation of a brown solid on the walls of the ozoniser, and equilibrium was attained when the residual gas contained 1 part of carbon dioxide to approximately 12 parts of the monoxide. Those experiments showed also that the composition of the brown solid, which was calculated from the results of analysis of the residual gases at equilibrium, varied with the initial pressure of the carbon monoxide, the ratio of carbon to oxygen increasing as the initial pressure of the monoxide diminished. In addition, it was found that the composition of the solid was independent of the potential applied to the ozoniser electrodes in the range examined, *viz.*, 4000—9000 volts.

Further experiments at the same frequency have now been carried out with the aim of more completely elucidating the nature of this substance. The apparatus has been modified in order to produce relatively large amounts, of the order of several grams, and to ensure that the "suboxide" should be formed at a constant partial pressure of the monoxide and in the absence of appreciable quantities of the dioxide. The conditions of formation are therefore more exactly defined than in the earlier experiments in which the carbon dioxide produced was not removed. Despite the improved technique, the preparation of the suboxide in quantity is a slow process, and is rendered difficult by a tendency to decompose spontaneously in air.

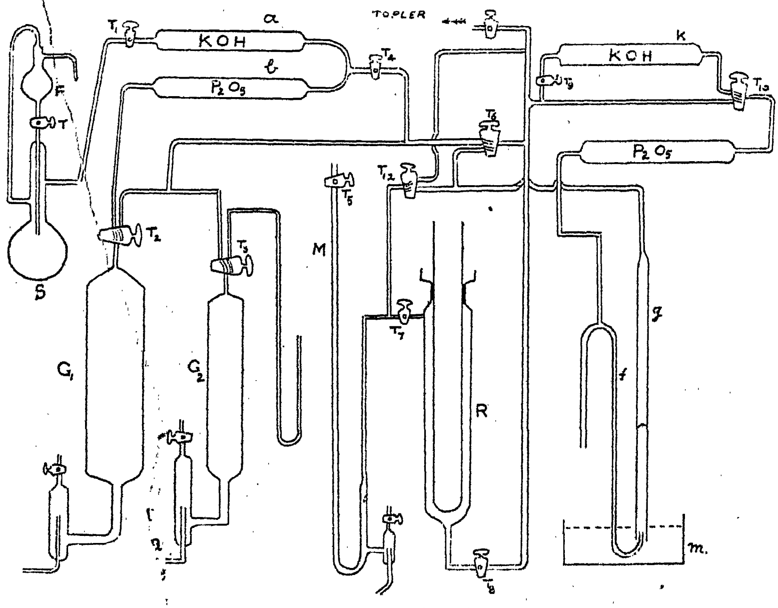
EXPERIMENTAL.

The electrical technique employed was identical with that described in Part I of this series.

Reaction Vessel.—The vessel which contained the gas while it was subjected to the discharge (Fig. 2) was that employed previously, *viz.*, a Siemens ozoniser constructed of glass, and connected to the auxiliary apparatus as represented in Fig. 1. The inner tube, t_1, was ground to fit the outer tube, t_2, at one end, thus facilitating the removal of any substance formed in the annular space between the tubes. It was filled with mercury, which served as the high-tension electrode, E_1. A glass tube containing mercury surrounded the outer tube and formed the low-tension electrode, E_2, which was earthed. The electrodes were water-cooled and their temperatures were recorded by alcohol thermometers. The external diameters of the two tubes of the reaction vessel were 25·5 and 15·2 mm., respectively, and the internal diameters were 23·3 and 12·7 mm., the thicknesses being thus 1·1 and 1·25 mm., respectively. The total volume included between the stopcocks was 81 c.c., and the effective length of the electrode was 33 cm.

An automatic Sprengel pump, *fg*, circulated the gas continuously through the discharge. The gas was led from the reaction vessel by the tap, T_8, through some 6 feet of tubing containing caustic potash, *K*, and then over phosphorus pentoxide to the fall tube, *g*, of the Sprengel pump. From the pump the gas flowed to the reaction vessel *via* the taps T_{12} and T_7. The circulating system was connected by the taps T_{12} and T_6 to gas holders containing the monoxide, G_1G_2, in such a manner that this could be fed in as rapidly as the dioxide was removed by the potash. In this way an approximately constant pressure was maintained in the gas subjected to the discharge. A mercury manometer, *M*, was attached to the system as before.

FIG. 1.



General diagram showing connexions of different parts of the apparatus.

Preparation of Carbon Monoxide.—The gas was produced free from oxygen by the method described previously, in which recrystallised formic acid contained in the bulb, *F*, was allowed to drop into an evacuated flask, *S*, containing warm concentrated sulphuric acid.

Procedure.—In order to facilitate the rapid formation of the suboxide, the highest available potential was employed in all experiments, *viz.*, 10,000 volts r.m.s.; the corresponding current varied slightly with the pressure from 9—10 milliamps.

The method adopted for preparing quantities of about 2 g. of the suboxide consisted in circulating carbon monoxide continuously through the reaction vessel until about 5 litres had been consumed, the potash tube for absorbing carbon dioxide being connected in the circulating system. The supply of monoxide was adjusted to maintain the pressure constant within ± 5 mm. Hg. After the discharge was stopped, the reaction vessel was disconnected from the circulating system and filled with dry air. The inner tube was then removed from the outer tube, and the suboxide scraped off as rapidly as possible on account of its very hygroscopic nature and transferred to a vacuum desiccator containing phosphorus pentoxide. As soon as the inner tube had been withdrawn, the grease was

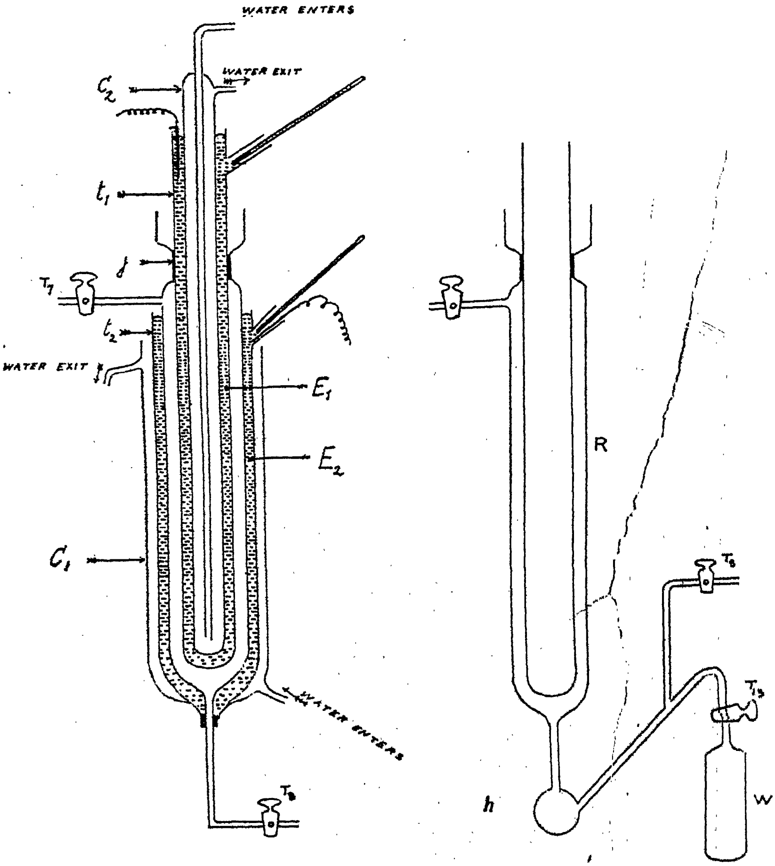


FIG. 2. FIG. 2A.

Reaction vessel.

removed from the ground joint of the outer tube, which was then filled with pure dry ether, and the solid adhering to the walls was loosened by rubbing with a clean dry copper rod. The ether and the solid were transferred to a flask and the former was removed by distillation, the residue being placed in a vacuum desiccator to remove the last traces of ether. The ether which had been in contact with the solid was not coloured, and on evaporation to dryness left no residue. The brown solid is therefore insoluble in ether, the use of which, to protect the solid from atmospheric contamination, would appear to be permissible.

In order to ascertain whether the conditions of experiment were substantially identical with those described in Part I, a fixed amount of carbon monoxide, at an initial pressure of 528·4 mm. Hg, was exposed to the discharge until equilibrium was reached, as indicated by the cessation of pressure change. The ratio of monoxide to dioxide in the residual gas was 11·4, which is in satisfactory agreement with the mean value, 11·58, previously obtained at an initial pressure of 501 mm. Hg.

Preliminary Examination of the Solid.—The experiments described in this section were carried out on the solid prepared by circulating carbon monoxide through the discharge at a constant pressure of 500 mm., the dioxide formed being removed continuously by potash. On treatment with water, the solid gave a brown, acidic solution having the smell of caramel, and a dark brown residue which was insoluble even in boiling water. Titration of this solution by standard alkali indicated that its acidity did not change with time. An examination of the solution under the ultramicroscope revealed the presence of colloidal particles. Prolonged boiling of the brown aqueous solution with purified animal charcoal did not decolorise it. The treatment of the solution with purified norit, freed from lime and silica, was more successful. Some five or six treatments with fresh norit were necessary, however, to give a nearly colourless solution. It was extremely tedious to prepare a colourless solution. The nitrates of aluminium, sodium, and thorium were also effective in partly decolorising the solution. Dialysis through a collodion membrane, although satisfactory in other ways, was too slow to be serviceable. The nearly colourless solution of the suboxide obtained by any of these methods was acid to litmus and reduced acidified potassium permanganate solution. When neutralised with ammonia the solution gave with calcium chloride a white, crystalline precipitate insoluble in acetic acid, and a white precipitate with silver nitrate, indicating that the original solution contained oxalic acid.

On concentrating the nearly decolorised solution of the brown solid obtained by treatment with norit, colourless crystals were obtained, m. p. 96—100° (m. p. of hydrated oxalic acid, 100°). Similar crystals were obtained by extracting with dry ether, in a Soxhlet apparatus, the solid remaining when the brown aqueous solution of the suboxide was evaporated to dryness. After recrystallisation from dry ether, colourless crystals were obtained which, alone or when mixed with pure hydrated oxalic acid, melted at 98—99°. The crystals were compared microscopically with those of oxalic, malonic, and succinic acids, and found to be very similar to the first. The *p*-toluidine derivative, after recrystallisation from absolute alcohol, had m. p. 265—266° (oxalo-*p*-toluidide melts at 266—267°).

The silver or calcium salt precipitated from the neutralised, nearly colourless solution of the brown solid carried with it the residual colouring matter in the solution. The silver salt thus obtained could not therefore be used to determine accurately the equivalent of the acid. It would appear, however, that ignition of the calcium salt leads to values for the oxalic acid content of the solution, but such data are reserved for a later communication The equivalent of the acid has, however, been determined by igniting the silver salt, dried at 100°, obtained from two different dialyses of a solution of the brown solid through a collodion membrane [Found : equiv., (*a*) 45·8, (*b*) 46·9. $(CO_2H)_2$ requires 45·0].

When the nearly colourless solution of the brown solid, obtained by treatment with norit, was titrated with permanganate, the end-points were indefinite, but this could not be traced to the effect of the norit. Since the brown, aqueous solution of the suboxide and the insoluble residue could be slowly and completely decolorised by acidified permanganate even in the cold, it would appear that the indefinite end-points might be due to the imperfect decoloration of the solution before titration. In view of the difficulty of obtaining a perfectly colourless solution and of the probable loss by adsorption on the norit, this method of decoloration was abandoned as unsuitable for further quantitative investigations. Nevertheless, a rough estimation was carried out and the results, although only approximate, are considered in the next section.

During attempts to scrape off the brown solid from the walls of the ozoniser, a curious phenomenon was observed on two occasions. The solid adhering to the outside of the inner tube was scraped with a nickel spatula into a glass basin. Almost immediately the solid in the basin glowed and gave off a white cloud with evolution of heat, and a dark, spongy mass resembling charcoal remained. When the contents of the basin were treated with water, the spongy mass floated and the water was not coloured, but was found to contain oxalic acid. It was thought that this curious phenomenon might have been due to the accidental presence of moisture on the spatula or in the glass basin. When the brown solid was treated with water or methyl alcohol, a gas containing carbon dioxide was evolved, accompanied by a hissing noise which was more pronounced in the case of methyl alcohol. In order to ascertain if the gas was entirely carbon dioxide, a small glass bulb, *h* (Fig. 2A), was inserted between the reaction vessel, *R*, and the tap, T_8. Through a side tube of the bulb, water could be distilled into it from the vessel *W*, containing air-free water, and by placing a beaker of hot water underneath the bulb the water from the bulb could be distilled into the ozoniser. After some brown solid had been formed in the ozoniser and the latter evacuated, water was distilled into it as described. The gas evolved was carbon dioxide with a trace of carbon monoxide.

It follows from these preliminary experiments that the brown solid on treatment with water produces carbon dioxide, a brown solution containing oxalic acid and colloidal particles, and an insoluble, brown residue.

Quantitative Examination of the Brown Solid.—In order to determine whether the composition of the solid, produced under the conditions already described, varied with the pressure of the monoxide as indicated by the earlier experiments (Part I), four samples prepared at 200, 350, 500, and 690 mm. were analysed by combustion in a stream of dry oxygen. The results showed that the substance contained carbon, hydrogen, and oxygen. Assuming that all the hydrogen in the material before combustion is present as water (possibly due to the absorption of atmospheric moisture during the transference from the reaction vessel and subsequent weighing), the atomic ratios of oxygen to carbon in the four samples of the brown solid were calculated to be, respectively, 0·58, 0·60, 0·60, and 0·59, each value being a mean of two determinations. There is thus a remarkable constancy in the ratio, corresponding to an empirical formula C_5O_3, throughout the range of pressure investigated; and it would appear that the compositions of the substances produced might be represented by the empirical formula C_5O_3,xH_2O. These conclusions suggest also that the product formed by streaming the gas through the discharge is not identical with that obtained from an enclosed mass of gas exposed to the discharge (compare Part I).

It has been mentioned that, under certain conditions, the brown solid reacts with water, evolving carbon dioxide. It was therefore necessary to determine whether any carbon dioxide was similarly evolved in the formation of the substance, C_5O_3,xH_2O, during the unavoidable hydration of the brown solid in manipulation. Analysis of samples of the solid, prepared at 500 mm., collected from the inner tube of the reaction vessel in the presence of moist air, and from the outer tube under dry ether, showed that the latter contained the smaller amount of water, as calculated from the hydrogen content; the results corresponded with the empirical formulæ $C_5O_3,1\cdot95H_2O$ and $C_5O_3,1\cdot65H_2O$, respectively. They show that the ratio of carbon to oxygen is constant and independent of the water content of the substance, and they therefore afford evidence that carbon dioxide had not been liberated during the hydration of the brown solid. Experiments are in progress to determine whether the hydrogen content of the solid can be traced solely to the absorption of atmospheric moisture, or if it is due, in part, to the liberation of water from the walls of the reaction vessel during the discharge.

The increase in weight which took place when a known amount of the solid was exposed to moist air at atmospheric pressure is given in Table I.

TABLE I.

(Initial weight of solid = 0·02848 g.)

Time of exposure (hrs.)	0·5	1·75	2·5	3·5	27	70
Total increase in weight (mg.)	5·4	8·8	12·6	15·4	15	15·2

The substance was treated subsequently with excess of water and the solution evaporated to dryness in a steam-oven; it had then suffered a total loss in weight of 0·00922 g., or 32·38%; 0·2427 g. of the same sample of brown solid, on direct treatment with water and subsequent evaporation to dryness, lost 0·0788 g., or 32·47% in weight. If it be assumed, in accordance with the experiments just described, that the increase in weight in moist air is due to the absorption of water only, then the observed increase corresponds to a change in composition from $C_5O_3,1\cdot70H_2O$ to $C_5O_3,4\cdot21H_2O$.

A further series of combustions was then carried out on samples obtained by treatment of the brown solid with water and subsequent evaporation to dryness in a steam-oven. The ratios of oxygen to carbon, computed as before, varied in an apparently chaotic manner with the pressure at which the brown solid had been formed. It would appear, however, that this erratic variation may be attributed to slow atmospheric oxidation of the suboxide residue after treatment with water and subsequent evaporation to dryness. Three successive combustions were carried out on the suboxide residue (original solid prepared at 200 mm.) so obtained, one in the forenoon, one in the afternoon, and the third on the next day. During this period the bulk of the substance, from which samples were taken for combustion, was exposed to the atmosphere in a steam-oven (100°). The results (Table II) show that whilst the proportion of hydrogen is fairly constant, that of oxygen progressively increases, indicating that the brown solid after treatment with water absorbs oxygen while in contact with the atmosphere at 100°. No precautions were taken, in the experiments in which chaotic results were obtained, to insure that such atmospheric oxidation was avoided, or that the time of drying in the steam-oven was constant.

TABLE II.

Sequence of experiments.	I.	II.	III.
Carbon	1·00	1·00	1·00
Hydrogen	0·77	0·78	0·78
Oxygen	0·66	0·69	0·71

The results of these combustion experiments may now be summarised. In the pressure range investigated, the brown solid, after treatment with water and subsequent evaporation to dryness in a steam-oven, yields a substance which contains carbon, hydrogen, and oxygen, and slowly absorbs oxygen in air at 100°, but no definite composition can be assigned to it until samples have been prepared under conditions such that the possibility of oxidation is excluded during the treatment with water and subsequent drying.

Some further experiments, in which the volume of the monoxide consumed in the discharge was measured, were carried out on the evolution of gas which takes place when the brown solid is treated with water. After the discharge had been discontinued, the reaction vessel was evacuated; air-free water was then distilled into the vessel in the manner already described. After ½ hour had elapsed, the gases formed were pumped out and analysed, the results obtained being given in Table III. In the experiment (see below) in which 16·05 c.c. of gas were thus obtained, a further quantity of water was distilled into the reaction vessel, and the gases were pumped out after ½ hour. Less than 0·1 c.c. of gas, which proved to be carbon dioxide, was obtained. Repetitions of this procedure over a period of 5 days resulted in the formation of 3·0 c.c. of carbon dioxide.

TABLE III.

Pressure of CO (mm.).	200.	350.	500.
Volume of CO consumed (c.c. at *N.T.P.*)	74·0	130·0	111·3
Volume of CO_2 formed (c.c. at *N.T.P.*)	10·55	19·05	16·05
Volume of CO formed (c.c. at *N.T.P.*)	0·30	0·25	0·60

These results suggest that there is a rapid reaction associated with the formation of carbon dioxide together with small amounts of the monoxide, and a slow reaction also producing carbon dioxide.

It is important to note that the volume of dioxide produced by the rapid reaction is very nearly 1/7th of the volume of the monoxide used in the formation of the brown solid.

The behaviour of the nearly colourless aqueous solution of the brown solid towards permanganate solution has already been described. By rapid titration with standard permanganate solution, two approximate determinations have been carried out on the amount of oxalic acid formed when the solid is dissolved in water. Two samples of the solid, prepared at 500 mm., were found by combustion to have the empirical compositions (*a*) $C_5O_3,1{\cdot}70H_2O$, (*b*) $C_5O_3,1{\cdot}69H_2O$. About 0·5 g. of the solid was dissolved in water, and the solution diluted to 100 c.c.; 20 c.c. of this solution were decolorised by 0·25 g. of norit, a little dilute sulphuric acid was added, and the solution was heated to boiling and titrated rapidly. The results showed that 0·6490 g. of (*a*) and 0·5178 g. of (*b*) yielded 0·1180 and 0·0933 g., respectively, of oxalic acid calculated as anhydride, C_2O_3. Titration of a solution containing a similar amount of pure oxalic acid, which had been treated in the above manner with norit, showed that 1% of the oxalic acid had been adsorbed by the norit. The values obtained above for the equivalent weight of oxalic anhydride in the solution are therefore probably low by this amount.

On the basis of the provisional hypothesis that the empirical formula C_5O_3,xH_2O can be assigned to the brown solid, the amounts of oxalic anhydride ($M = 72$) which are equivalent to 1 g.-mol. of "C_5O_3" contained in the brown solid used in the above experiments are calculated to be (*a*) 25·22 g., and (*b*) 24·93 g., *i.e.*, approximately 3 mols. of empirical composition C_5O_3,xH_2O react with water to give 1 mol. of oxalic acid. Since the empirical composition of the solid is represented by C_5O_3,xH_2O, and since the hydrogen content must arise from the absorption of water by one or both of the processes already mentioned, it would appear that the formation of the brown solid may be represented by the equation $7CO = C_5O_3 + 2CO_2$. It will be recalled that in the reaction between water and the brown solid in the reaction vessel approximately 1 vol. of carbon dioxide was liberated for every 7 vols. of monoxide consumed in producing the solid. This observation suggests (the small amount of monoxide formed at the same time being neglected) that in the reaction with water each mol. of "C_5O_3" reacts forming 1 mol. of carbon dioxide.

By combining the results obtained from combustion, from titration of the nearly decolorised aqueous solution, and from the reaction with water, the following equation is advanced tentatively to represent the action of water on the brown solid after it has been removed from the reaction vessel and exposed for a short time to atmospheric moisture:

$3C_5O_3,xH_2O + aq. = (CO_2H)_2 + 3CO_2 + 10C + (3x - 1)H_2O + aq.$

The production of free carbon, according to this equation, would account for the readiness with which the substance absorbs oxygen after treatment with water. Experiments are now in progress to determine the nature of the insoluble material formed when the brown solid is treated with water, and will form the subject of a future contribution.

Summary.

(1) A preliminary quantitative investigation has been carried out on the properties of the substance formed when carbon monoxide, at pressures from 200 to 690 mm. Hg, is subjected to ionisation by collision when streamed through an alternating electric field of the order of 20,000 volts per cm., and of frequency 250 cycles per sec.

(2) After removal from the reaction vessel, the substance has the empirical composition C_5O_3,xH_2O.

(3) The substance reacts with water, forming carbon dioxide, a brown solution containing oxalic acid and colloidal particles, and a dark, insoluble residue.

The authors wish to express their indebtedness to the Royal Commissioners of 1851 for a Senior Studentship which has enabled one of them (R. W. L.) to continue this research, and particularly to Professor F. G. Donnan, F.R.S., for his deep interest and advice during the development of this work.

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CXXVII.—*The Vapour Pressure of Intensively Dried Nitrogen Tetroxide.*

By JOHN WILLIAM SMITH.

THE following experiments were commenced in 1925 with a view to extend the researches on the effect of intensive drying on physical properties. At that time, the only work on nitrogen tetroxide which had been carried out in this direction was due to H. B. Baker and Mrs. Baker (J., 1912, **101**, 2339), who had found that material which had been dried for more than a year boiled above 60°, whereas the normal b. p. is 22°, but no claim to great accuracy was made for this result on account of the small quantity of liquid available.

When the present work was nearly complete, however, a communication on the same subject was published by Smits and his collaborators (J., 1926, 2657), who found that the vapour pressure of nitrogen tetroxide, unlike that of systems previously investigated, rises on intensive drying. The results of the present work, obtained quite independently, confirm those of Smits and extend them in certain directions.

EXPERIMENTAL.

Preparation of Materials.—The nitrogen tetroxide was prepared by the method of Cundall (J., 1891, **59**, 1077) in a modified form of the apparatus used by Ray (*J. Physical Chem.*, 1925, **29**, 74). It was redistilled four times in dry oxygen and stored in sealed tubes over phosphorus pentoxide.

The phosphorus pentoxide was resublimed in pure dry oxygen in a horizontal tube of "Durosil" glass, with a side tube at the end remote from the oxygen inlet. This side tube was arranged to give a good sliding fit into the U-tube or other receiver for the sublimed material. Thus only a very narrow channel was left to allow the oxygen to escape, thereby preventing any access of moisture. The tube was well dried by passing dry oxygen through it whilst hot. It was charged by the tube-and-ramrod method described by Baker (*Phil. Trans.*, 1888, *A*, **179**, 573), with the oxygen current passing in the opposite direction. Sufficient material was introduced to eliminate the necessity of recharging during the sublimation process. The inlet tube was then inserted and the receiver slipped over the side tube. The phosphorus pentoxide was heated to 300° in a current of oxygen. Under these conditions, it sublimed steadily, condensing on the cooler part of the tube in light, feathery crystals, which were transferred to the receiver by turning a spiral rake.

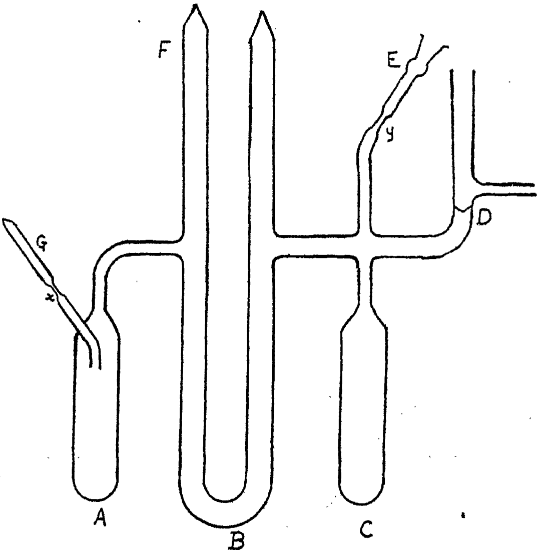
Drying Apparatus.—For a more complete investigation of the properties of intensively dried nitrogen tetroxide, it was essential to secure a more rapid method of drying than that used heretofore. For this purpose, a slightly modified form of the apparatus used by Smits and Schoenmaker in their work on sulphur trioxide (J., 1924, **125**, 2554) was adopted. This was made of selected "Durosil" glass, as free as possible from streaks and air bubbles. The drying apparatus (Fig. 1) consisted of two bulbs, *A* and *C*, connected by a U-tube, *B*. The upper part of the tube from *C* ended in a tube, *E*, which could be connected to a high-vacuum pump system through a ground glass joint, whilst a side tube led to a sealed-in glass septum, *D*.

Procedure.—After thorough cleaning, all tubes except *E* were sealed off, and *E* was connected to the vacuum-pump system. Whilst under a high vacuum, the whole apparatus was maintained at 300° for 2 days. Dry air was now admitted, and tube *E* rapidly closed.

The end of tube *F* was cut off, and phosphorus pentoxide sublimed in, as already described. Careful tapping caused the pentoxide to pass round the bend into the further limb of the U-tube. In this way, *B* was filled almost completely in about 3 hours. With the oxygen current still passing, tube *F* was drawn off. Tube *G* was then reopened, and nitrogen tetroxide introduced from a storage bulb, bulb *A* being simultaneously cooled. Tube *G* was sealed off again at the constriction *x*. The tetroxide was then cooled in liquid air, *E* being connected again to the vacuum-pump system. Tube *E* was finally sealed off at the constriction *y* under a high vacuum. The tetroxide was then allowed to become warm. Distillations were carried out by immersing one bulb in ice and the other in water at room temperature, the baths being reversed every few hours.

Experiment 1.—In this case distillations were carried out for 4 months. The time necessary for a complete distillation, about 3 hours at the outset, gradually increased as drying proceeded. Meanwhile a vapour-pressure apparatus was constructed of the form shown in Fig. 2. This consisted essentially of a long tube carrying a series of small bulbs provided with constrictions, and a bulb, *J*, to contain phosphorus pentoxide. One end of this long tube was connected to the inside of an all-glass pressure gauge of one of the forms described by Jackson (J., 1911, **99**, 1066). The outer jacket of this gauge was connected to a mercury manometer and to the vacuum-pump system. The two sides of the gauge were at first connected through a tube, *L*, with a constriction suitable for vacuum sealing. A breaker, consisting of a piece of stout capillary tubing with a short piece of soft iron inside, was now placed on the septum, *D*, of the drying apparatus. The tube *M* was then sealed to the T-piece above the septum, as shown in the diagram, and the vertical tube above the septum sealed off. The apparatus was now

FIG. 1.



evacuated to a pressure of 10^{-6} mm., the whole apparatus up to the septum being heated almost to softening point for 2 days. The top of the tube from *J* was then cut off, resublimed phosphorus pentoxide rapidly introduced, and the tube drawn off again. The evacuation and heating were then repeated for some days. The capillary, *L*, was sealed off while still under a high vacuum, and the apparatus allowed to stand for a few days. Meanwhile, the gauge was calibrated by admitting air to its outer sheath. The movement of the needle of the gauge with reference to a fixed pointer, *R*, was observed through a fixed cathetometer.

The nitrogen tetroxide was finally brought into bulb *C*, where it was frozen out in solid carbon dioxide and alcohol. The breaker was then lifted by means of an electromagnet and dropped to break the septum, thus putting the nitrogen tetroxide vapour in contact with the pressure gauge. The temperature of the tetroxide was gradually allowed to rise, the pressure being roughly balanced by admitting air to the outer sheath of the gauge. The pressure was read off on the mercury gauge, fine corrections being calculated from the deflexion of the glass gauge from the normal. In this way, the vapour pressure was determined over the range 0—15°, giving the results shown in Table I.

Fig. 2.

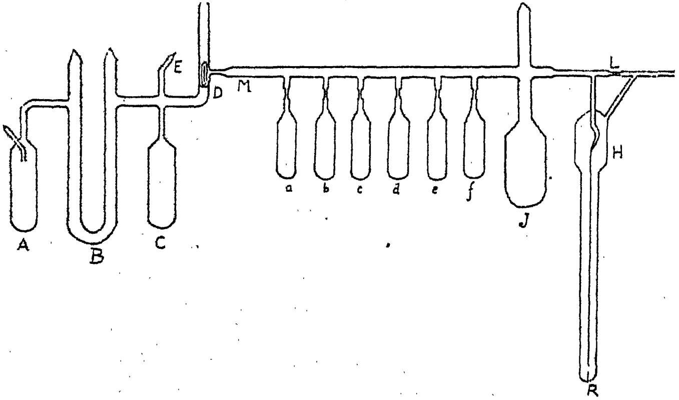


TABLE I.

	Vapour pressures (mm.).				Vapour pressures (mm.).		
Temp.	Dry.	Wet.	Change.	Temp.	Dry.	Wet.	Change.
0·0°	266·3	264·0	+2·3	12·1°	493·7	489·5	+4·2
1·8	292·1	290·3	+1·8	14·6	559·5	554·2	+5·3
8·5	411·8	408·2	+3·6	15·0	571·2	565·0	+6·2

The values given under the heading "wet" were obtained by the author, using an apparatus of the type described above, with nitrogen tetroxide that had been dried for a week over phosphorus pentoxide. The results agreed very well with the values obtained by Scheffer and Treub (*Z. physikal. Chem.*, 1912, **81**, 308).

The results with the dried material all tend to show a slight rise. There are, however, a few irregularities. These were explainable after the more thoroughly dried material had been examined in Expt. 2.

Bulb *f* was then slowly cooled in a freezing mixture and finally in solid carbon dioxide and alcohol. In this way, the nitrogen tetroxide in the gauge and tubes, presumably the more volatile portion, was condensed, and slow distillation occurred from the liquid in *C*. When about 5 c.c. had condensed, *C* was also cooled in carbon dioxide and alcohol, and bulb *f* sealed off. The temperature was again allowed to rise and the vapour pressure redetermined. This operation was repeated with bulbs *e* and *d*, the vapour pressure of the residue being taken on each occasion. The results are shown in Table II.

TABLE II.

No. of fraction removed.	Temp.	Vapour pressures (mm.). Dry.	Wet.	Change.
1	0·0°	265·3	264·0	+1·3
	14·7	560·4	557·3	+3·1
2	0·0	264·6	264·0	+0·6
	14·6	558·6	554·2	+4·4
3	0·0	263·1	264·0	−0·9
	14·7	561·0	557·3	+3·7

It would appear from these results that little, if any, separation of a more volatile from a less volatile component had been effected by this means.

Expt. 2.—The apparatus and method of drying employed were exactly the same as in the previous case, but the pressure-gauge portion was somewhat simplified, and made very much more compact, the fractionating bulbs being dispensed with. Thus this portion of the apparatus could be baked out much more readily than in the previous case. The whole apparatus, up to and including the glass spring gauge, was enclosed in a large air-thermostat during the pressure determination. The technique employed was similar to that in the previous case. In this apparatus there was only about one-half as much nitrogen tetroxide as in Expt. 1, whilst there was rather more phosphorus pentoxide. It had been drying for about 6 months, and during this time had been distilled to and fro nearly 400 times.

In order to obtain a full series of results before any possible reversion to the normal form could occur, the whole temperature range 0—30° was explored in one day. All the results tended to show a distinct rise in the vapour pressure, but there were certain marked anomalies. It was found that although the apparatus was kept at constant temperature for more than an hour, the vapour pressure continued to rise, this rise being so slow that it was not at first noticed. Hence the time which had been allowed at each temperature for a constant vapour pressure to be established (about ½ hour) was clearly quite insufficient, although 10 minutes had sufficed with the undried material in a similar apparatus and under similar conditions. The value of the apparent "initial" vapour pressure, and also the rate of the change, seemed to depend on the previous history of the system. Thus, after the tetroxide had been frozen out in carbon dioxide and alcohol, the vapour pressure at 0° was some 6 hours in attaining a constant value, whilst the apparent "initial" vapour pressure was much greater when the liquid had only been cooled to about —10°. Hence the vapour pressures were determined at a few temperatures by allowing long periods for attainment of equilibrium; the results are in Table III.

TABLE III.

	Vapour pressures (mm.).				Vapour pressures (mm.).		
Temp.	Dry.	Wet.	Change.	Temp.	Dry.	Wet.	Change.
0·0°	282·6	264	+19	20·5°	757·9	736	+22
5·2	370·3	348	+22	24·2	890·5	869	+21
15·2	595·8	571	+25	24·7	910·3	890	+20
15·9	615·4	591	+24	29·0	1100·5	1080	+20
19·6	727·8	704	+24				

These values were all obtained about 10 days after the septum had been broken, when the vapour pressure at 0° appeared to remain steady. Some idea of the rate of reversion to the normal form was obtained by taking the vapour pressure at 0° on different days. This value fell from 286·8 mm. on the second day after breaking the septum to 282·6 mm. on the tenth day, *i.e.*, a drop in the abnormality from 23 to 19 mm. This slight reversion was apparently caused by the slow diffusion of moisture out of the less completely dried gauge portion of the apparatus.

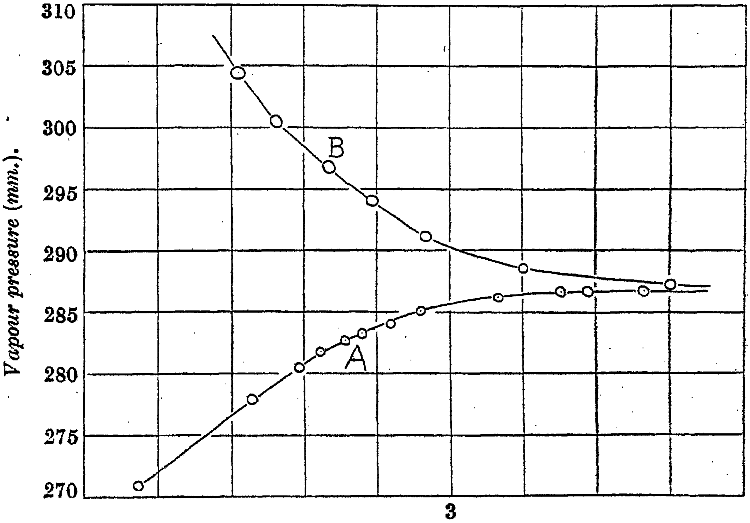
That these rises in the vapour pressure were not due to any leakage in the apparatus during the 6 months' drying was shown by freezing out the nitrogen tetroxide in liquid air, whereupon no residual gas pressure was observed.

The slow establishment of a steady vapour pressure was further investigated. The liquid was cooled to about —10° for some 3 hours, and then immersed in pure ice and water, which was stirred continuously. Readings were taken at frequent intervals during 4 hours. The corresponding readings were also taken after the system had been cooled from 12° to 0°. The vapour pressure-time curves are shown in Fig. 3. These values were obtained on the second day after breaking the septum.

The high vapour pressures obtained and this slow change in the vapour pressure on standing at constant temperature seem to indicate that the equilibrium is shifted by the intensive drying, but at the stage when it was examined it was not completely fixed. Hence, when the temperature was raised, a corresponding, but slow, change occurred in the inner equilibrium, a less volatile component passing into a more volatile one. It would be natural to suppose that intensive drying would affect the known inner equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, but it is not possible to say, from the experiments recorded in this paper, to what extent changes in this equilibrium might account orthe observed phenomena.

FIG. 3.

Vapour pressure–time curves at 0°.



Time (hours).

A. *After cooling to* —10°.
B. *After heating to* 19·6°.

Some indication of the form of a constant composition–vapour pressure curve was obtained by reaching equilibrium at one temperature, and then warming quickly to another temperature. These values can only be taken as approximate, however, as it is difficult to separate the two factors—ordinary thermal equilibrium and inner equilibrium. Two examples of the type of result obtained are given in Table IV. These values were obtained by reaching equilibrium at the temperature given in the first column, immersing the liquid in a bath at the temperature shown in the second column, and taking the vapour pressure after 15 minutes.

TABLE IV.

Temp. at which equilibrium was attained.	Temp. of measurement.	Vapour pressure (mm.).		
		After thermal equilibrium was established.	Normal.	Change.
0·0°	0·0°	282·6	264	+19
	9·4	437·2	428	+ 8
	12·6	505·2	503	+ 2
5·4	5·4	373·1	351	+22
	14·9	562·6	562	+ 0·6

Summary.

(*a*) It has been shown that after intensive drying at room temperature the vapour pressure of nitrogen tetroxide is increased throughout the range 0—30°.

(*b*) In accordance with the view developed by Smits, this would suggest a shift in the inner equilibrium towards the side of a more volatile component.

(*c*) The vapour pressure took a considerable time to reach a constant value. This is attributed to slow internal changes in the system, consequent upon temperature change.

In conclusion, I desire to express my indebtedness to the Tuffnell Trustees for a Scholarship, to the Department of Scientific and Industrial Research for a grant, and especially to Professor F. G. Donnan, F.R.S., at whose suggestion this work was carried out, for his kindly advice and criticism throughout the progress of the research.

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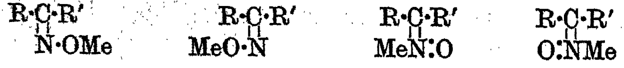
PHYSICAL CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, February* 11*th*, 1927.]

CXXVIII.—*The Isomerism of the Oximes. Part XXIX. Isomeric* p-*Nitrobenzyl and Methyl Ethers of Some Aldoximes.*

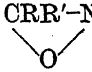
By OSCAR L. BRADY and LOUIS KLEIN.

THE Hantzsch–Werner theory demands the existence of two isomeric *O*-ethers and two isomeric *N*-ethers corresponding to a pair of isomeric unsymmetrical oximes.



$$\begin{matrix}R\cdot C\cdot R' \\ \| \\ N\cdot OMe\end{matrix} \qquad \begin{matrix}R\cdot C\cdot R' \\ \| \\ MeO\cdot N\end{matrix} \qquad \begin{matrix}R\cdot C\cdot R' \\ \| \\ MeN{:}O\end{matrix} \qquad \begin{matrix}R\cdot C\cdot R' \\ \| \\ O{:}NMe\end{matrix}$$

The Beckmann structural theory as extended by Atack (J., 1921, **119**, 1175) demands one *O*-ether and two *N*-ethers,



$$\mathrm{CRR'{:}N{\cdot}OMe},\quad \underset{\diagdown\,O\,\diagup}{\mathrm{CRR'{-}NMe}},\quad \mathrm{CRR'{:}NMe{:}O}.$$

Four isomeric methyl ethers have been obtained from certain unsymmetrical ketoximes (Semper and Lichtenstadt, *Ber.*, 1918, **51**, 928; Plowman and Whiteley, J., 1924, **125**, 587; Brady and Mehta, *ibid.*, p. 2297) but, despite many attempts, only one *N*-ether has been obtained from any one aldoxime (Brady, Dunn, and Goldstein, J., 1926, 2386). Now the gravamen of Atack's charge against the Hantzsch–Werner theory was the paucity of evidence for the existence of two isomeric *O*-ethers of undoubted composition. The best authenticated cases are the pairs of *O*-methyl ethers of *p*-nitrobenzophenoneoxime (Brady and Mehta, *loc. cit.*), *m*-nitrobenzaldoxime, and 3-nitro-4-methoxybenzaldoxime (Goldschmidt, *Ber.*, 1890, **23**, 2170; Brady and Dunn, J., 1913, **103**, 1620; Brady, Dunn, and Goldstein, J., 1926, 2402). In other cases, one or both of the isomerides are uncrystallisable oils (methyl ethers of *p*-tolylphenoximes, benzaldoximes, *p*-methoxy- and *o*-nitro-benzaldoximes), or the unstable is much more fusible than the stable isomeride and a mixture of the two melts at an intermediate temperature, so there is no satisfactory criterion of purity of the lower-melting compound (methyl, ethyl, and benzyl ethers of *p*-nitrobenzaldoximes). Even the evidence that the α- and β-*O*-methyl-*m*-nitrobenzaldoximes * are truly *O*-ethers is not entirely satisfactory.

The objects of the work here presented were (1) to adduce further evidence of the constitution of the two *O*-methyl-*m*-nitrobenzaldoximes, (2) the preparation of a number of pairs of *O*-ethers from various oximes, and (3) a further search for a second *N*-ether of aldoximes. The last effort was unavailing and no evidence was obtained of the existence of more than one *N*-ether corresponding to any one aldoxime. It has been found that both *O*-methyl-*m*-nitrobenzaldoximes have normal molecular weights and give quantitative yields of methyl iodide when heated with hydriodic acid. Further, a mixture of the two *O*-ethers has been obtained by the action of *O*-methylhydroxylamine on *m*-nitrobenzaldehyde, the α-isomeride greatly preponderating.

The evidence for the constitution of these compounds as *O*-ethers is therefore (1) methoxyl determinations, (2) synthesis from *O*-methylhydroxylamine, (3) partial conversion of the α- into the β-form by ultra-violet light (Brady and McHugh, J., 1924, **125**,

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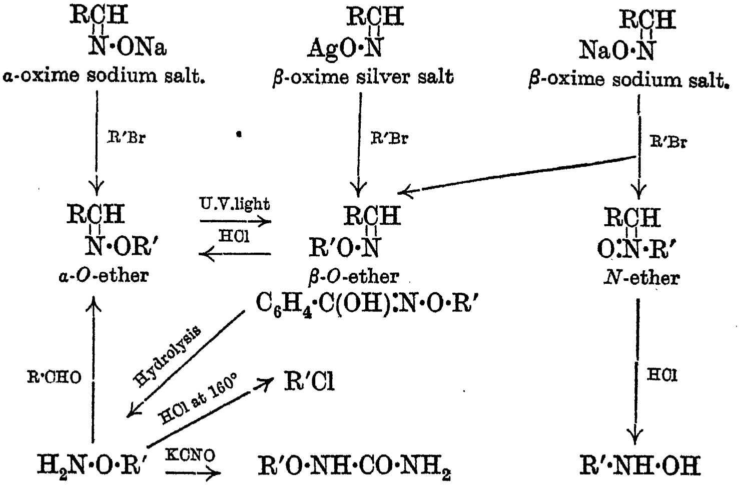
* The nomenclature used in this paper is that suggested by Brady and Bishop (J., 1925, **127**, 1361), and the new configurations have been adopted.

552), (4) complete conversion of the β- into the α-form by hydrogen chloride at room temperature (Goldschmidt and Kjellin, *Ber.*, 1891, **24**, 2555) and (5) normal molecular weights. None of this evidence rules out the structure RCH—N suggested as possible although

)Me

unlikely by Atack, who states that a substance having this structure should be readily convertible into the more stable form, >C:N·O·R. He has overlooked the rather surprising stability of the β-*O*-ethers in the absence of acids; *e.g.*, β-*O*-methyl-*m*-nitrobenzaldoxime is not isomerised on melting and can be kept unchanged for 16 years, whereas β-*m*-nitrobenzaldoxime is completely converted into the α-isomeride after 4 years. Moreover, the isomeric *O*-methyl-*p*-nitrobenzophenoneoximes are not interconvertible by means of hydrogen chloride (Brady and Mehta, *loc. cit.*). The ring formula is, however, inadmissible until some evidence is adduced for the existence of compounds of this type in which none of the four oxygen valencies is attached to a negative group—the compounds instanced by Atack (Kehrmann and Bohn, *Ber.*, 1914, **47**, 3052) are all salt-like in structure.

The chief difficulty experienced in previous work on the ethers of the aldoximes was the low melting point of the methyl, ethyl, and benzyl compounds and for this reason the *p*-nitrobenzyl derivatives have been studied, since compounds containing this radical have usually a higher melting point. As a result, three isomeric ethers, derived from each of ten pairs of isomeric oximes, have been prepared. One of the three was an *N*-ether as shown by its ready hydrolysis by acids to the aldehyde and *N*-*p*-nitrobenzylhydroxylamine and by its synthesis from these two compounds, the constitution of the latter of which was proved by Behrend and Leuchs and by Behrend and König (*Annalen*, 1890, **257**, 243; 1891, **263**, 190). The other two were *O*-ethers. This was established as follows. The previously unknown O-p-*nitrobenzylhydroxylamine* was prepared by the hydrolysis of *O*-*p*-nitrobenzylbenzhydroxamic acid (Werner, *Ber.*, 1892, **25**, 44), and its constitution proved by its conversion into *p*-nitrobenzyl chloride by heating under pressure with hydrochloric acid, by its reaction with potassium cyanate to give *p*-nitrobenzyloxycarbamide and by its failure to reduce cold Fehling's solution. This compound reacted with aldehydes, giving ethers identical with those obtained by the action of *p*-nitrobenzyl bromide on the sodium salts of the α-aldoximes, *i.e.*, the α-*O*-ethers. In six cases these α-*O*-ethers were converted by ultra-violet light into the β-*O*-ethers identical with those obtained by the action of *p*-nitrobenzyl bromide on the silver salts of the β-aldoximes. In all ten cases the β-*O*-ethers were completely converted into the α-*O*-ethers by hydrogen chloride. These changes may be represented diagrammatically thus, R′ denoting $NO_2{\cdot}C_6H_4{\cdot}CH_2$:



The α-*O*-ethers are very stable towards hydrolysing agents, being unchanged by boiling with aqueous or alcoholic hydrochloric acid, hydrobromic acid, 60% sulphuric acid or 2*N*-sodium hydroxide.

The sodium salts of the α-oximes gave with *p*-nitrobenzyl bromide almost exclusively α-*O*-ethers; in only one case could any indication of the formation of the *N*-ether be detected (compare Brady, Dunn, and Goldstein, *loc. cit.*; Brady and Goldstein, J., 1926, 2403). The sodium salts of the β-oximes gave mainly the *N*-ethers, but small quantities of the β-*O*-ethers were also obtained in five cases. The β-*O*-ethers were generally prepared by the action of (1) *p*-nitrobenzyl bromide on either the β-aldoxime in the presence of dry silver oxide, or the silver salt of the β-aldoxime, (2) ultra-violet light on the α-*O*-ethers. The results are summarised in Table I.

As the melting points of the two isomeric *O*-ethers are frequently close together, the melting point of a mixture of approximately equal amounts of the two is given also; the figure for the two *O*-ethers of *p*-methoxybenzaldoxime is the m. p. of a mixture prepared by adding a very small quantity of the α- to the β-*O*-ether. That the β-*O*-ethers have been prepared by various methods is further evidence of their entity; a particular method was, however, not always equally successful and in some cases failed altogether.

The cases of Nos. 5 and 9 are of special interest, since all attempts to obtain the β-oximes have been unsuccessful (Brady and Dunn, J., 1923, **123**, 1787; Brady and Manjunath, J., 1924, **125**, 1066);

TABLE I.

p-Nitrobenzyl Ethers of Aldoximes.

	Oxime.	M. p. of *N*-ether.	M. p. of α-*O*-ether.	M. p. of β-*O*-ether.	Mixed m. p. of α- + β-*O*-ethers.	Methods of preparation of β-*O*-ethers.
1	Benzaldoxime	110°	60—61°	54°	37—38°	Ag salt.
2	*o*-Nitrobenzaldoxime	203	112	116	94—95	Ag_2O; Na salt; U.V. light.
3	*m*-Nitrobenzaldoxime	223	87—88	118	77—79	Ag_2O; Ag salt; Na salt; U.V. light.
4	*p*-Nitrobenzaldoxime	234—235	179	184	153—155	Ag_2O; Ag salt; Na salt; U.V. light.
5	*o*-Methoxybenzaldoxime	141	88	Oil.	—	U.V. light.
6	*p*-Methoxybenzaldoxime	150	122	74	69—70	Ag salt; Na salt; U.V. light.
7	3 : 4-Methylenedioxybenzaldoxime	144	110	125	95	Ag_2O; Ag salt; U.V. light.
8	3-Nitro-4-methoxybenzaldoxime	232	117	152	108—109	Ag_2O; Ag salt; Na salt; U.V. light.
9	5-Nitro-2-methoxybenzaldoxime	237	149	153	128—130	U.V. light.
10	Cinnamaldoxime	135	83	86	62—63	Ag_2O.

the U.V. light method was therefore the only one available for the preparation of the β-*O*-ethers. It is noteworthy that conversion occurs although U.V. light has no action upon the parent oximes (compare Brady and McHugh, J., 1924, **125**, 552, and experimental part). α-*O*-Methyl-6-nitro-3 : 4-methylenedioxybenzaldoxime also has been partly converted into the β-form by similar means ; only one form of the oxime is known.

The *N*-ethers of *o*-methoxy- and 5-nitro-2-methoxy-benzaldoximes were obtained from the aldehydes and *N*-*p*-nitrobenzylhydroxylamine, since the β-oximes are unknown.

The action of *p*-nitrobenzyl bromide on the sodium salt of β-cinnamaldoxime produced a viscous, brown oil which could not be purified. The *N*-ether was, however, easily prepared by the action of *N*-*p*-nitrobenzylhydroxylamine on the aldehyde. It behaved abnormally on hydrolysis, giving a product which could not be satisfactorily purified. This peculiar behaviour is being further investigated (compare Bamberger and Weitnauer, *Ber.*, 1922, **55**, 3376).

The *N*-*p*-nitrobenzyl ethers undergo the Beckmann change in the same way as the *N*-methyl ethers (Brady and Dunn, J., 1926, 2411).

Finally the binary fusion diagram for α-benzaldoxime and *p*-nitrobenzyl bromide was constructed, but no evidence of compound formation was forthcoming (compare Brady and Truszkowski, J., 1924, **125**, 1089 ; Brady and Klein, J., 1925, **127**, 852).

We consider that the results here described remove all doubt of the existence of two isomeric *O*-ethers. Any theory of the isomerism of the oximes must therefore provide for two such compounds and, so far, only that suggested by Hantzsch and Werner makes a serious attempt to do so.

EXPERIMENTAL.

Action of p-*Nitrobenzyl Bromide on Sodium Salts of α-Aldoximes.*

α-Benzaldoxime.—The oxime (8 g.) dissolved in alcohol (20 c.c.) was mixed with sodium ethoxide (from 1·53 g. of sodium in 40 c.c. of alcohol), and a hot solution of *p*-nitrobenzyl bromide (14·4 g.) in alcohol (100 c.c.) added. Having been heated on the water-bath for ½ hour, the mixture was diluted with water (250 c.c.) and cooled in ice. The α-*O*-*p*-nitrobenzylbenzaldoxime thus obtained, in 89% yield, crystallised from alcohol in almost white prisms, m. p. 60—61° (Found: N, 11·1; *M*, cryoscopic in benzene, 253. Calc.: N, 10·9%; *M*, 256). Schroeter and Peschkes (*Ber.*, 1900, **33**, 1982) described the compound as forming yellow prisms. The ether was unaffected by boiling with hydrochloric acid (aqueous or alcoholic), hydrobromic acid, 60% sulphuric acid or with sodium hydroxide solution.

The aqueous-alcoholic filtrate from the above preparation was extracted with chloroform, and the extract was washed with 2*N*-sodium hydroxide, to remove unchanged oxime, and with water, evaporated to small bulk, and dried over sodium sulphate. Treatment with dry hydrogen chloride for an hour produced a small precipitate (m. p. 172—173°) of *N*-*p*-nitrobenzylhydroxylamine hydrochloride, decomposition of which with aqueous sodium carbonate gave a small quantity of *N*-*p*-nitrobenzylhydroxylamine (m. p. 120°), identified by comparison with an authentic specimen.

α-Cinnamaldoxime.—By the above method (oxime, 2·72 g. in 15 c.c. of alcohol; sodium ethoxide from 0·43 g. of sodium and 20 c.c. of alcohol; *p*-nitrobenzyl bromide, 4 g. in 40 c.c. of alcohol) a 69% yield was obtained of α-O-p-*nitrobenzylcinnamaldoxime*, which crystallised from alcohol in buff leaflets, m. p. 83° (Found: N, 10·2; *M*, cryoscopic in benzene, 271. $C_{16}H_{14}O_3N_2$ requires N, 9·9%; *M*, 282).

*α-*o*-Nitrobenzaldoxime.*—Owing to the sensitiveness of this oxime to hot alkali, the reaction was carried out at room temperature. The oxime (5 g.) in 30 c.c. of cold alcohol was treated with sodium ethoxide (from 0·7 g. of sodium and 30 c.c. of alcohol), a warm solution of *p*-nitrobenzyl bromide (6·5 g. in 80 c.c. of alcohol) added, and the mixture immediately cooled; a yellow solid then separated. After 12 hours, the precipitate was collected (84% yield), and crystallised from alcohol, α-O-p-*nitrobenzyl*-o-*nitrobenzaldoxime* being obtained in pale yellow leaflets, m. p. 112° (Found: N, 13·9; *M*, cryoscopic in camphor, 295. $C_{14}H_{11}O_5N_3$ requires N, 14·0%; *M*, 301).

The alcoholic filtrate from the preparation was diluted and treated as described under benzaldoxime, but nothing crystalline was isolated.

α-m-*Nitrobenzaldoxime*.—The oxime (8 g., suspended in 25 c.c. of alcohol), sodium ethoxide (from 1·11 g. of sodium and 40 c.c. of alcohol), and *p*-nitrobenzyl bromide (10·4 g. in 75 c.c. of hot alcohol) were heated on the water-bath under reflux for 30 minutes. On cooling, an oil separated which soon solidified (yield 90%). This crystallised from alcohol containing a little acetone, α-O-p-*nitrobenzyl*-m-*nitrobenzaldoxime* being obtained in pale yellow prisms, m. p. 87—88° (Found : N, 14·1 ; *M*, cryoscopic in benzene, 284. $C_{14}H_{11}O_5N_3$ requires N, 14·0% ; *M*, 301). The compound is dimorphous, for when its concentrated alcoholic solution is slowly cooled without stirring, pale yellow prisms, m. p. 97°, are obtained and a solution of these in hot alcohol, on being cooled rapidly and stirred, deposits the lower-melting form. A mixture of approximately equal amounts of either form with β-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime melts at 77—79°.

α-p-*Nitrobenzaldoxime*.—The O-p-*nitrobenzyl ether*, prepared similarly to the *m*-compound in 88% yield, crystallises from acetone in glistening, pale yellow prisms, m. p. 179° (Found : N, 13·9. $C_{14}H_{11}O_5N_3$ requires N, 14·0%).

α-3 : 4-*Methylenedioxybenzaldoxime*.—The addition of *p*-nitrobenzyl bromide (10·5 g. in 100 c.c. of hot alcohol) to a solution of the oxime (8 g. in 60 c.c. of warm alcohol) mixed with sodium ethoxide (from 1·12 g. of sodium and 40 c.c. of alcohol) gave a precipitate which dissolved when the mixture was heated under reflux for 30 minutes. On cooling, a mass of yellow crystals separated and, after dilution with a little water, these were collected (yield 96%) and crystallised from acetone; α-O-p-*nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* was then obtained in pale yellow prisms, m. p. 110° (Found : N, 9·4; *M*, cryoscopic in camphor, 315. $C_{15}H_{12}O_5N_2$ requires N, 9·3% ; *M*, 300).

α-p- *and* α-o-*Methoxybenzaldoximes*.—Treated as described above with sodium ethoxide (from 0·92 g. of sodium and 40 c.c. of alcohol) and *p*-nitrobenzyl bromide (8·58 g. in 80 c.c. of alcohol), these oximes (6 g. in 50 c.c. of alcohol) gave, respectively, an 84% yield of α-O-p-*nitrobenzyl*-p-*methoxybenzaldoxime*, pale yellow prisms from acetone, m. p. 122° (Found : N, 9·7. $C_{15}H_{14}O_4N_2$ requires N, 9·8%), and a 79% yield of α-O-p-*nitrobenzyl*-o-*methoxybenzaldoxime*, very pale yellow prisms from methyl alcohol, m. p. 88° (Found : N, 9·9%).

α-3-*Nitro*-4-*methoxy*- *and* α-5-*Nitro*-2-*methoxy*-*benzaldoximes*.—Treated as described above with sodium ethoxide (from 0·59 g. of sodium and 30 c.c. of alcohol) and *p*-nitrobenzyl bromide (5·51 g.

in 35 c.c. of hot alcohol), the oximes (5 g. in 40 c.c. of alcohol) gave, respectively, a 90% yield of α-O-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime,* a pale yellow, micro-crystalline powder from amyl alcohol, m. p. 117° (Found: N, 12·8; *M*, cryoscopic in camphor, 340. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331), and an 87% yield of α-O-p-*nitrobenzyl*-5-*nitro*-2-*methoxybenzaldoxime*, white, micro-crystalline needles from acetone, m. p. 149° (Found: N, 12·7%; *M*, cryoscopic in camphor, 328).

α-*O*-*p*-Nitrobenzyl-3-nitro-4-methoxybenzaldoxime is dimorphous like the derivative from *m*-nitrobenzaldoxime, separating from benzene in yellow prisms, m. p. 105°.

O-p-*Nitrobenzylhydroxylamine.*

Benzhydroxamic Acid.—Jeanrenaud (*Ber.*, 1889, **22**, 1272) obtained this compound in 40% yield, but more than 60% can be obtained by the following modification of his process. Hydroxylamine hydrochloride (23·2 g.) was dissolved in the minimum amount of water, and alcohol (50 c.c.) added followed by alcoholic sodium ethoxide (7·7 g. of sodium in 180 c.c. of alcohol). The precipitated sodium chloride was filtered off, and ethyl benzoate (50 g.) added followed by more sodium ethoxide (7·7 g. of sodium in 180 c.c. of alcohol). On cooling, the liquid set to a mass of crystals of sodium benzhydroxamate, which were collected, washed with alcohol, dried, and dissolved in the minimum of water. The solution was acidified with hydrochloric acid and extracted six times with chloroform; the extract on evaporation yielded benzhydroxamic acid sufficiently pure for the next preparation.

O-p-*Nitrobenzylbenzhydroxamic Acid,* $C_6H_5{\cdot}C(OH){:}N{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$ or $C_6H_5{\cdot}CO{\cdot}NH{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$. —A solution of benzhydroxamic acid (25 g.) in alcohol (80 c.c.) was mixed with a solution of potassium hydroxide (10·2 g.) in water (40 c.c.), *p*-nitrobenzyl bromide (39·4 g. in 300 c.c. of hot alcohol) added, and the mixture heated under reflux for 45 minutes. On cooling, *O*-*p*-nitrobenzylbenzhydroxamic acid separated and was crystallised from alcohol (compare Werner, *Ber.*, 1892, **25**, 44).

O-p-*Nitrobenzylhydroxylamine.*—*O*-*p*-Nitrobenzylbenzhydroxamic acid (15 g.) in hot alcohol (125 c.c.) was boiled under reflux for 25 minutes with concentrated hydrochloric acid (150 c.c.). The clear solution thus obtained was cooled somewhat and diluted with water (150 c.c.) and while still warm was extracted with chloroform (200 c.c.) to remove benzoic acid, etc. The extraction was carried out as rapidly as possible, since, when the liquid cooled, the sparingly soluble *O*-*p*-nitrobenzylhydroxylamine hydrochloride was apt to separate. The aqueous layer was evaporated to dryness on the water-bath; a 96% yield of the crude compound was then obtained. The residue was crystallised from hot 2*N*-hydrochloric acid and the crystals were washed with alcohol and then with ether, pure O-p-*nitrobenzylhydroxylamine hydrochloride* being obtained in white leaflets, m. p. 217° (decomp.) (Found: Cl, 17·9. $C_7H_8O_3N_2,HCl$ requires Cl, 17·3%). Boiling with water produces partial hydrolysis, and, unlike *N*-*p*-nitrobenzylhydroxylamine, the compound does not reduce Fehling's solution. The hydrochloride was dissolved in a little hot water, containing hydrochloric acid, and a solution of potassium cyanate added; p-*nitrobenzyloxycarbamide* separated on cooling and crystallised from hot water in white prisms, m. p. 206° (decomp.) (Found: N, 20·1. $C_8H_9O_4N_3$ requires N, 19·9%).

O-*p*-Nitrobenzylhydroxylamine hydrochloride (0·5 g.) was heated in a sealed tube at 160—180° for 4 hours with concentrated hydrochloric acid (2 c.c.). After cooling, the liquid contained a few colourless plates of the unchanged compound and some brown lumps; the latter were crystallised from light petroleum, and the *p*-nitrobenzyl chloride thus obtained was identified by comparison with an authentic specimen and by conversion into *p*-nitrobenzyl iodide by boiling in alcohol with potassium iodide. The hydrochloric acid mother-liquor on evaporation yielded ammonium chloride. When a concentrated solution of the hydrochloride in hot water, containing hydrochloric acid, was poured with stirring into an excess of 2*N*-sodium carbonate, an emulsion was obtained which, on cooling in ice, deposited crystals of the free base; a further quantity was obtained by extracting the mother-liquor with chloroform. After crystallising from light petroleum containing a little benzene, O-p-*nitrobenzylhydroxylamine* was obtained in white prisms, m. p. 56° (Found: N, 16·9. $C_7H_8O_3N_2$ requires N, 16·7%).

Action of O-p-*Nitrobenzylhydroxylamine on Aldehydes.*

p-Nitrobenzaldehyde (1·5 g.) in hot alcohol was treated with a solution of *O*-*p*-nitrobenzylhydroxylamine hydrochloride (2 g.) in hot 2*N*-hydrochloric acid (20 c.c.); crystals of α-*O*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime soon began to separate. After cooling, they were collected and washed with alcohol (yield 2 g.).

By similar methods, like results were obtained with *o*-nitrobenzaldehyde, 5-nitro-2-methoxybenzaldehyde, and 3 : 4-methylenedioxybenzaldehyde, except that in the last case the mixture was heated for a short time on the water-bath.

m-Nitrobenzaldehyde (0·9 g.) in warm alcohol (15 c.c.) was mixed with a solution of *O*-*p*-nitrobenzylhydroxylamine (1·05 g.) in warm alcohol (12 c.c.); after 3 days, crystals of α-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime had separated (yield 1·6 g.). The alcoholic mother-liquor was fractionally precipitated with water, but only a small amount of the α-*O*-ether was obtained and there was no indication of the presence of the β-*O*-ether. The α-*O*-ethers were similarly obtained from cinnamaldehyde and *p*-methoxybenzaldehyde and *O*-*p*-nitrobenzylhydroxylamine. In every case the *O*-ether was identified by the method of mixed melting points with that obtained by the action of *p*-nitrobenzyl bromide on the sodium salt of the α-oxime.

Action of Silver Oxide and p-*Nitrobenzyl Bromide on* β-*Aldoximes.*

β-*Cinnamaldoxime.*—The oxime (2·94 g.) and *p*-nitrobenzyl bromide (4·32 g.) were dissolved in hot benzene (30 c.c.), dry, finely powdered silver oxide (2·6 g.) was added, and the mixture was boiled under reflux for an hour. After silver oxide and bromide had been removed, the solution was allowed to evaporate spontaneously. The residual solid was pressed on a porous tile, washed with 2*N*-sodium hydroxide to remove unchanged oxime and with water, and crystallised twice from methyl alcohol; β-O-p-*nitrobenzylcinnamaldoxime* was then obtained in pale buff prisms, m. p. 86° (yield 1·5 g.) (Found: N, 10·0; *M*, cryoscopic in benzene, 280. $C_{16}H_{14}O_3N_2$ requires N, 9·9%; *M*, 282).

β-o- *and* β-m-*Nitrobenzaldoximes.*—The finely powdered oxime (1 g.) and *p*-nitrobenzyl bromide (1·3 g.) were dissolved in benzene (75 c.c.) at room temperature, dry silver oxide (1 g.) was added, and the mixture was kept for 5 days in the dark in a corked flask with occasional shaking. The mixture was then heated to boiling and filtered hot. The filtrate on spontaneous evaporation gave a sticky solid which, after being pressed on a porous tile and crystallised four times from alcohol, yielded β-O-p-*nitrobenzyl*-o-*nitrobenzaldoxime* in feathery needles, m. p. 116° (Found: N, 13·7; *M*, cryoscopic in camphor, 312. $C_{14}H_{11}O_5N_3$ requires N, 14·0%; *M*, 301). Similarly, β-O-p-*nitrobenzyl*-m-*nitrobenzaldoxime* was obtained, crystallising from methyl alcohol in white leaflets, m. p. 118° (Found: N, 14·0%; *M*, cryoscopic in ethylene dibromide, 326).

β-p-*Nitro- and* β-3 : 4-*Methylenedioxy-benzaldoximes.*—The finely powdered oxime (3 g.) and *p*-nitrobenzyl bromide (3·9 g.) were suspended in benzene (250 c.c.) at room temperature, dry silver oxide (3 g.) was added, and the mixture was kept in the dark in a corked flask for 6 days with occasional shaking. After being heated to boiling and filtered, the solution gave on evaporation a solid which was washed with 2*N*-sodium hydroxide, water, and a little warm acetone. The residue on crystallisation from acetone gave β-O-p-*nitrobenzyl*-p-*nitrobenzaldoxime* as a white, micro-crystalline powder,

m. p. 184° (Found : N, 13·8. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). Similarly, β-O-p-*nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* was obtained in yellow prisms, m. p. 125° (Found : N, 9·5; *M*, cryoscopic in camphor, 325. $C_{15}H_{12}O_5N_2$ requires N, 9·3%; *M*, 300).

β-3-*Nitro*-4-*methoxybenzaldoxime*.—By a similar method to the preceding, from the oxime (2·7 g.), *p*-nitrobenzyl bromide (2·97 g.), benzene (500 c.c.), and silver oxide (1·9 g.), β-O-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* was obtained; it crystallised from alcohol–acetone in white needles, m. p. 152° (Found : N, 12·8; *M*, cryoscopic in camphor, 348. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331).

β-*Benzaldoxime and* β-p-*Methoxybenzaldoxime*.—β-Benzaldoxime gave only an uncrystallisable oil by the silver oxide method. β-*p*-Methoxybenzaldoxime gave only the α-*O*-*p*-nitrobenzyl ether, although various solvents and other modifications of procedure were tried. The β-*O*-ethers from these two oximes have, however, been prepared by another method (see below).

Action of p-*Nitrobenzyl Bromide on Silver Salts of* β-*Aldoximes.*

β-*Benzaldoxime,* β-p-*Methoxy-,* β-p-*Nitro-, and* β-3-*Nitro*-4-*methoxy-benzaldoximes*.—The silver salts were each prepared by suspending the oxime in alcohol, adding an alcoholic solution of sodium ethoxide prepared from a weighed quantity of sodium, shaking the mixture until a clear solution was obtained, and then adding in artificial light an aqueous-alcoholic solution of silver nitrate. The precipitated silver salt, which was usually difficult to filter off, was collected and washed first with absolute alcohol and then with dry chloroform. The quantities used for β-benzaldoxime, β-*p*-methoxybenzaldoxime, β-*p*-nitrobenzaldoxime and β-3-nitro-4-methoxybenzaldoxime, respectively, were oxime (7·2 g.; 5·5 g.; 1·45 g.; 4·35 g.), alcohol (50 c.c.; 50 c.c.; 20 c.c.; 60 c.c.), sodium (1·37 g. in 70 c.c. of alcohol; 0·83 g. in 50 c.c.; 0·2 g. in 15 c.c.; 0·51 g. in 30 c.c.), silver nitrate (11 g. in the minimum of water, and 80 c.c. of alcohol added; 6·5 g., and 75 c.c. of alcohol; 2 g., and 15 c.c. of alcohol; 4 g., and 30 c.c. of alcohol). The silver salt so obtained was suspended in a solution of *p*-nitrobenzyl bromide in chloroform and kept in a corked flask in the dark for a week with occasional shaking. The quantities were *p*-nitrobenzyl bromide (9 g.; 4 g.; 1·3 g.; 3·2 g.), chloroform (100 c.c.; 45 c.c.; 30 c.c.; 55 c.c.) respectively. The solution was then filtered, and the chloroform allowed to evaporate spontaneously. In the case of β-benzaldoxime, great difficulty was experienced at first in inducing the residual oil to crystallise. This was overcome by seeding the oil with a little of the crude product of the action of *p*-nitrobenzyl bromide on the sodium salt of β-benzaldoxime and keeping it in an evacuated desiccator for a week in an ice-chest; the pasty mass thus obtained was pressed on a porous tile. Later, when the pure β-*O*-ether was available, it was sufficient to seed the oil with this, keep it as before for 2 days, and press the solid on a tile. In this way, 3·6 g. of a nearly pure product were obtained. On crystallising from alcohol with seeding, β-O-p-*nitrobenzylbenzaldoxime* was obtained in pale yellow crystals, m. p. 54° (Found: N, 11·1; *M*, cryoscopic in benzene, 247. $C_{14}H_{12}O_3N_2$ requires N, 10·9%; *M*, 256). Similarly, after crystallising from acetone and water and then from methyl alcohol, β-O-p-*nitrobenzyl*-p-*methoxybenzaldoxime* was obtained in fine, white needles, m. p. 74° (Found: N, 9·9. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

The addition of a small amount of α-*O*-*p*-nitrobenzyl-*p*-methoxybenzaldoxime (m. p. 122°) lowered the melting point of the above compound to 69°; with somewhat larger quantities of the α-ether, the mixed melting point lay between 74° and 122°. The β-*O*-*p*-nitrobenzyl ethers of *m*-nitro-, *p*-nitro-, 3 : 4-methylenedioxy-, and 3-nitro-4-methoxy-benzaldoximes were prepared analogously from the silver salts of the respective β-oximes and found to be identical with the compounds obtained from these oximes by the silver oxide method.

Action of Ultra-violet Light on α-O-p-*Nitrobenzyl Ethers.*

The method consisted in exposing a solution of the α-*O*-*p*-nitrobenzyl ether in benzene in a silica vessel to the light of a quartz mercury-vapour lamp at a distance of about 5 inches. The exposure was usually continuous for 72 hours. The benzene was then removed and the crude product, after its melting point had been determined, was fractionally crystallised from suitable solvents. Unless the contrary is mentioned, the products were identified by the method of mixed melting points with ethers otherwise prepared, mixed melting points being taken with both α- and β-ethers.

α-O-p-*Nitrobenzyl*-o-*nitrobenzaldoxime* (m. p. 112°; 1 g. in 25 c.c. of benzene).—The crude product (m. p. 91—92°) was dissolved in the minimum of boiling alcohol; on cooling, crystals, m. p. 99—101°, separated which, on recrystallisation from alcohol, gave unchanged α-*O*-ether. The mother-liquor from the first crystallisation, on being diluted somewhat with water and scratched, gave crystals (m. p. 97—106°) which, recrystallised three times from alcohol, gave the pure β-*O*-ether (m. p. 116°).

α-O-p-*Nitrobenzyl*-m-*nitrobenzaldoxime* (m. p. 87—88°; 1·5 g. in 25 c.c. of benzene).—The crude product (m. p. 73—77°) was dissolved in a small quantity of hot alcohol, containing a little acetone, and the solution cooled with stirring; the product, m. p. 76—78°, thus obtained crystallised from a fairly large volume of alcohol, containing a little acetone, a compound, m. p. 103—104°, being obtained which, after two crystallisations from methyl alcohol, yielded the pure β-*O*-ether (m. p. 118°).

α-O-p-*Nitrobenzyl*-p-*nitrobenzaldoxime* (m. p. 179°; 2 g. in 150 c.c. of benzene).—The crude product (m. p. 150—151°) was treated with boiling acetone, partial solution occurring. The solution was decanted while hot, and the residue, after two crystallisations from much acetone, gave the pure β-*O*-ether (m. p. 184°). The acetone extract, on cooling, gave crystals (m. p. 156—158°) which, after repeated crystallisation from acetone, gave more β-*O*-ether. The mother-liquor from the crystals (m. p. 156—158°) was diluted with water and the precipitate produced was crystallised from acetone; the pure α-*O*-ether was then obtained.

α-O-p-*Nitrobenzyl-3 : 4-methylenedioxybenzaldoxime* (m. p. 110°; 1 g. in 40 c.c. of benzene; exposure, 68 hours).—The residue (m. p. 75—90°), after being pressed on a porous tile and washed with a little ether, was dissolved in a hot mixture of alcohol and acetone, and the solution, after cooling, was fractionally precipitated with water. The first and the second fraction, after crystallisation from acetone and water and then from acetone, gave unchanged α-*O*-ether. The third fraction, m. p. 80—85°, crystallised from acetone and water and then from alcohol, gave a very small quantity of somewhat impure β-*O*-ether (m. p. 120°).

α-O-p-*Nitrobenzyl*-p-*methoxybenzaldoxime* (m. p. 122°; 1·5 g. in 45 c.c. of benzene; exposure, 100 hours).—The residue (m. p. 100—105°), on crystallisation from acetone, gave unchanged α-*O*-ether; addition of a little water to the acetone filtrate gave another crop of this compound. The aqueous-acetone filtrate, on spontaneous evaporation, yielded a pasty solid which was pressed on a porous tile and crystallised twice from methyl alcohol; a very small yield of β-*O*-ether was then obtained.

α-O-p-*Nitrobenzyl-3-nitro-4-methoxybenzaldoxime* (m. p. 117°; 0·75 g. in 45 c.c. of benzene).—The crude product (m. p. 115—126°) was crystallised from benzene and then twice from acetone–alcohol, the pure β-*O*-ether being obtained. The benzene mother-liquor gave only impure β-*O*-ether.

α-O-p-*Nitrobenzyl*-o-*methoxybenzaldoxime* (m. p. 88°; 1·5 g. in 25 c.c. of benzene; exposure, 100 hours).—The crude product (m. p. 78—80°), on crystallisation from alcohol, gave the α-*O*-ether; a second crop of the same compound was obtained by diluting the filtrate with a little water. The aqueous-alcoholic filtrate, on spontaneous evaporation, gave an oil which would not crystallise on being seeded with the α-*O*-ether. It undoubtedly contained the

unknown β-*O*-ether, for, after hydrogen chloride had been passed into its chloroform solution and the solvent evaporated, the residue immediately solidified on being scratched and was then found to be almost pure α-*O*-ether (compare below).

α-O-p-*Nitrobenzyl-5-nitro-2-methoxybenzaldoxime* (m. p. 149°; 3 g. in 150 c.c. of benzene; exposure, 96 hours).—The crude product (m. p. 123—126°) was dissolved in 40 c.c. of boiling acetone and, after cooling, fractionally precipitated with water. The first fraction (m. p. 132—139°), after three crystallisations from acetone–alcohol, gave 0·5 g. of β-O-p-*nitrobenzyl-5-nitro-2-methoxybenzaldoxime* in white needles, m. p. 153° (Found: N, 12·8; *M*, cryoscopic in camphor, 357. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331). Admixture with the α-*O*-ether caused a depression of melting point to 128—130°.*

Action of Hydrogen Chloride on β-O-p-*Nitrobenzyl Ethers.*

Hydrogen chloride was passed for 10—20 seconds into a solution of a small quantity of the β-*O*-ether in a little chloroform. The solution was then evaporated, and the product (after crystallisation from alcohol in the case of the ether of cinnamaldoxime) identified as the corresponding α-*O*-ether by the method of mixed melting points. From the ether of benzaldoxime an oil was obtained which, however, immediately solidified on being seeded with a crystal of the α-*O*-ether. With the ethers of *m*-nitro- and 3-nitro-4-methoxybenzaldoximes the oils obtained solidified on being rubbed with a little alcohol. The results are in Table II.

TABLE II.

	Before HCl treatment.		After HCl treatment.		
O-*p*-Nitrobenzyl ether of	M. p.	Mixed m. p. with α-*O*-ether.	M. p.	Mixed m. p. with α-*O*-ether.	M. p. of α-*O*-ether.
β-Cinnamaldoxime	86°	62—63°	77—79°	81—82°	83°
β-Benzaldoxime	54	37—38	57—58	59	60—61
β-*o*-Nitrobenzaldoxime	116	94—95	107—108	110—111	112
β-*m*-Nitrobenzaldoxime	118	77—79	82—83	85—86	87—88
β-*p*-Nitrobenzaldoxime	184	153—155	174—175	177—178	179
β-3 : 4-Methylenedioxybenzaldoxime	125	95	105	107	110
β-*p*-Methoxybenzaldoxime	74	69—70	115—117	119—120	122
β-3-Nitro-4-methoxybenzaldoxime	152	108—109	105—106	111—112	117
β-*o*-Methoxybenzaldoxime	Oil.	—	74—76	78—80	88
β-5-Nitro-2-methoxybenzaldoxime	153	128—130	146	148	149

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* Exposure of a benzene solution of α-5-nitro-2-methoxybenzaldoxime to ultra-violet light for 48 hours did not result in its conversion into the β-isomeride.

Action of p-*Nitrobenzyl Bromide on Sodium Salts of* β-*Aldoximes.*

The general method was to suspend the β-oxime in alcohol and add a solution of sodium ethoxide in alcohol (the oxime then dissolved as the sodium salt) followed by a warm solution of *p*-nitrobenzyl bromide in alcohol. The mixture was at once cooled in running water and then treated as described below.

β-*Benzaldoxime* (6 g. in 25 c.c.; 1·14 g. of sodium in 40 c.c.; 10·71 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After being kept for 24 hours, the solution was diluted with water and cooled in ice with stirring. The yellow solid thus obtained was washed with water, dried in the air, and crystallised three times from small quantities of benzene, giving *N*-*p*-nitrobenzylbenzaldoxime, m. p. 110° (Found : N, 11·3. Calc. : N, 10·9%) (compare Behrend and König, *loc. cit.*). No β-*O*-ether could be isolated from the benzene mother-liquors.

The *N*-ether (1 g. in 20 c.c. of benzene) was exposed to ultra-violet light for 54 hours and the solvent was then removed; the residue had a faint odour of benzaldehyde or benzonitrile and consisted practically entirely of unchanged *N*-ether (compare Brady and McHugh, J., 1924, **125**, 553).

N-*p*-Nitrobenzylbenzaldoxime (1 g.) and pure acetic anhydride (5 c.c.) were gently heated together. A somewhat vigorous reaction occurred at the boiling point, and the liquid was immediately cooled, poured into excess of 2*N*-sodium carbonate, and shaken for some time until the odour of the anhydride disappeared. The solid that separated, after being washed with water and crystallised from alcohol, was found to be benzo-*p*-nitrobenzylamide by comparison with an authentic specimen. This amide has been described by Hafner (*Ber.*, 1890, **23**, 339), but several improvements in the method of preparation have been devised. Phthal-*p*-nitrobenzylimide (0·5 g.), prepared from potassium phthalimide and *p*-nitrobenzyl bromide (Hammick and Locket, J., 1922, **121**, 2362; Salkowski, *Ber.*, 1889, **22**, 2142), was heated under reflux for 4 hours with 60% sulphuric acid (30 c.c.)—an improvement on Gabriel's method (*Ber.*, 1887, **20**, 2227). After cooling, the liquid was diluted with water, made alkaline with sodium hydroxide, and extracted with chloroform. The liquid *p*-nitrobenzylamine obtained on removal of the solvent was suspended in 2*N*-sodium hydroxide (30 c.c.) and shaken with benzoyl chloride (1 c.c.) for 30 minutes. The precipitated benzo-*p*-nitrobenzylamide was collected and crystallised from alcohol.

β-o-*Nitrobenzaldoxime* (4 g. in 25 c.c.; 0·56 g. of sodium in 30 c.c.; 5·2 g. of *p*-nitrobenzyl bromide in 50 c.c. of alcohol).—After 12 hours, the yellow precipitate was collected, washed with a little alcohol, dried (yield, 3·7 g.; m. p. 170—175°), and extracted with warm ether; this removed 0·3 g. of material which, after crystallisation from alcohol, gave β-*O*-*p*-nitrobenzyl-*o*-nitrobenzaldoxime. The portion insoluble in ether, after three crystallisations from acetone, gave N-p-*nitrobenzyl*-o-*nitrobenzaldoxime* in long, pale yellow prisms, m. p. 203° (decomp.) (Found: N, 14·1. $C_{14}H_{11}O_5N_3$ requires N, 14·0%).

β-m-*Nitrobenzaldoxime* (7 g. in 30 c.c.; 0·97 g. of sodium in 50 c.c.; 9·11 g. of *p*-nitrobenzyl bromide in 120 c.c. of alcohol).—After 12 hours, the precipitate was collected, washed with alcohol and dried (yield, 12 g.; m. p. 215—218°). Crystallised from boiling glacial acetic acid, it gave N-p-*nitrobenzyl*-m-*nitrobenzaldoxime* in canary-yellow prisms, m. p. 223° (decomp.), which were very sparingly soluble in most organic solvents (Found: N, 14·2. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). The alcoholic filtrate from the *N*-ether was largely diluted with water and after 12 hours 0·6 g. of impure β-*O*-ether had separated (m. p. 90—103°). This was extracted with hot methyl alcohol, a little insoluble *N*-ether separated, and the filtrate cooled and diluted with water. The precipitated compound was pressed on a porous tile, washed with a little ether, and crystallised from methyl alcohol; pure β-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime was then obtained.

β-p-*Nitrobenzaldoxime* (5·42 g. in 60 c.c.; 0·75 g. of sodium in 30 c.c.; 7·05 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After 12 hours, the precipitate was washed with alcohol, dried (yield, 9·8 g.; m. p. 216—221°), and extracted with boiling acetone. The filtered extract was evaporated on the water-bath, leaving a solid residue. This was boiled with acetone, and the cooled, filtered solution was diluted with water, producing a precipitate which, crystallised from acetone and water and then twice from acetone, gave a very small quantity of β-*O*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime. The residue from the first acetone extraction, after crystallisation from boiling pyridine, gave *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, m. p. 234—235° (decomp.). This compound was prepared by Behrend and König (*loc. cit.*) by the oxidation of *NN′*-di-*p*-nitrobenzylhydroxylamine. They give m. p. 227—228°, and we have found that this is the maximum melting point attainable if acetic acid or nitrobenzene, the solvents used by those authors, is employed for crystallisation.

β-3 : 4-*Methylenedioxybenzaldoxime* (3·3 g. in 40 c.c.; 0·46 g. of sodium in 30 c.c.; 4·32 g. of *p*-nitrobenzyl bromide in 60 c.c. of alcohol).—The solid was crystallised from acetone and water and then twice from acetone–alcohol, N-p-*nitrobenzyl*-3 : 4-*methylene*-

dioxybenzaldoxime being obtained in deep canary-yellow leaflets, m. p. 144° (Found: N, 9·3. $C_{15}H_{12}O_5N_2$ requires N, 9·3%). No β-*O*-ether could be isolated from the various mother-liquors.

β-p-*Methoxybenzaldoxime* (7·65 g. in 60 c.c.; 1·17 g. of sodium in 60 c.c.; 10·94 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After 24 hours, water (700 c.c.) was added to the mixture, and the precipitated solid was collected and air-dried (yield, 13·85 g.; m. p. 90—100°). After two crystallisations from acetone, N-p-*nitrobenzyl*-p-*methoxybenzaldoxime* was obtained in yellow needles, m. p. 150° (Found: N, 9·8. $C_{15}H_{14}O_4N_2$ requires N, 9·8%). The acetone mother-liquor from the first crop of crystals of the *N*-ether gave, on dilution, a further crop of *N*-ether. The aqueous-acetone filtrate was allowed to evaporate spontaneously and the solid obtained was extracted with boiling ether (100 c.c.), some *N*-ether remaining undissolved. Light petroleum (75 c.c.) was added to the solution; a sticky precipitate was then obtained which was rejected. The ether–light petroleum filtrate, on evaporation in a current of air, gave 0·9 g. of material which yielded, after crystallisation from methyl alcohol, β-*O*-*p*-nitrobenzyl-*p*-methoxybenzaldoxime.

β-3-*Nitro*-4-*methoxybenzaldoxime* (3·55 g. in 40 c.c.; 0·42 g. of sodium in 30 c.c.; 3·91 g. of *p*-nitrobenzyl bromide in 40 c.c. of alcohol).—After 12 hours, the yellow precipitate was collected (yield 6 g.) and crystallised twice from acetone, giving N-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* in bright yellow needles, m. p. 232° (decomp.) (Found: N, 12·8. $C_{15}H_{13}O_6N_3$ requires N, 12·7%). The acetone mother-liquor from the first crystallisation was evaporated to dryness, and the residue extracted with boiling chloroform. The extract was separated from undissolved *N*-ether and evaporated to dryness; the residue (0·8 g.), after two crystallisations from alcohol–acetone, gave β-*O*-*p*-nitrobenzyl-3-nitro-4-methoxybenzaldoxime.

Hydrolysis of N-p-*Nitrobenzyl Ethers.*

N-*p*-Nitrobenzyl-*p*-methoxybenzaldoxime (4·3 g.) was triturated with 160 c.c. of concentrated hydrochloric acid; the mixture was then boiled under reflux for an hour, diluted with a little water, cooled, and extracted with chloroform. The extract, on evaporation, gave an oil which was identified as *p*-methoxybenzaldehyde by conversion into the semicarbazone, the yield of this compound being 2·8 g. (calc., 2·9 g.). The aqueous layer was evaporated to dryness on the water-bath; the *N*-*p*-nitrobenzylhydroxylamine hydrochloride that remained (yield, 2·7 g.; calc., 3·1 g.), on crystallisation from absolute alcohol by addition of ether, gave the pure compound, m. p. 179—181° (compare Behrend and König, *Annalen*, 1891, 263, 190). By addition of 2*N*-sodium carbonate to a concentrated aqueous solution of the hydrochloride, the free base was obtained, m. p. 120—122° after crystallisation from hot water (Behrend and König, *loc. cit.*). This method of preparing *N*-*p*-nitrobenzylhydroxylamine from *p*-methoxybenzaldoxime *N*-*p*-nitrobenzyl ether is preferable to that described by the above authors, since β-*p*-methoxybenzaldoxime is one of the easiest β-aldoximes to obtain pure and in quantity and the *N*-*p*-nitrobenzyl ether is more easily hydrolysed than that of *p*-nitrobenzaldoxime owing to the very sparing solubility of the latter.

The *N*-*p*-nitrobenzyl ethers of benzaldoxime, 3 : 4-methylenedioxy-, *o*-methoxy-, and 5-nitro-2-methoxy-benzaldoximes were hydrolysed in an analogous way; benzaldehyde and *o*-methoxybenzaldehyde were identified as semicarbazones and 3 : 4-methylenedioxy- and 5-nitro-2-methoxy-benzaldehydes as α-oximes.

N-*p*-Nitrobenzyl-*m*-nitrobenzaldoxime (8 g.) was triturated with 200 c.c. of boiling concentrated hydrochloric acid, and steam was rapidly passed through the mixture for 5 hours. The distillate on extraction with chloroform gave 3·9 g. of *m*-nitrobenzaldehyde (calc., 4·0 g.). The liquid in the flask on evaporation to dryness on the water-bath gave 5·2 g. of crude *N*-*p*-nitrobenzylhydroxylamine (calc., 5·4 g.), which was identified as before.

The *N*-*p*-nitrobenzyl ethers of *o*- and *p*-nitro- and 3-nitro-4-methoxy-benzaldoximes were hydrolysed similarly to the *m*-nitro-derivative. In the case of *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, hydrobromic acid proved more satisfactory than hydrochloric acid. 3-Nitro-4-methoxybenzaldehyde was obtained as an oil and identified by conversion into the α-oxime.

Action of N-p-*Nitrobenzylhydroxylamine on Aldehydes.*

An alcoholic solution of the aldehyde was treated successively with alcoholic solutions of *N*-*p*-nitrobenzylhydroxylamine hydrochloride and potassium acetate, and the mixture kept for a definite time.

Cinnamaldehyde (1·9 g. in 4 c.c.; *N*-*p*-nitrobenzylhydroxylamine hydrochloride, 3·2 g., in 24 c.c.; potassium acetate, 2 g., in 20 c.c.). —After 12 hours, the precipitate was washed with a little alcohol and with water; 2·6 g. were then obtained. A further crop of 1·4 g. was obtained by diluting the mother-liquors.

N-p-*Nitrobenzylcinnamaldoxime* crystallises from benzene in lemon-yellow needles, m. p. 135° (Found: N, 9·9. $C_{16}H_{14}O_3N_2$ requires N, 9·9%). This compound could not be prepared by the action of *p*-nitrobenzyl bromide on the sodium salt of β-cinnamaldoxime, the products under various conditions being brown tars from which nothing crystalline could be isolated. On hydrolysis with hydrochloric acid, the *N*-ether behaved abnormally, giving a yellow, crystalline substance mixed with a resinous material from which it could not be separated.

o-*Methoxybenzaldehyde* (0·5 g. in 5 c.c.; hydrochloride, 0·83 g., in 5 c.c.; acetate, 0·5 g., in 5 c.c. of alcohol).—0·72 G. of crude *N*-ether crystallised and a further 0·12 g. was obtained by diluting the mother-liquor. N-p-*Nitrobenzyl*-o-*methoxybenzaldoxime* crystallises from alcohol in very pale yellow, fern-like crystals, m. p. 141° (Found : N, 10·2. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

5-*Nitro-2-methoxybenzaldehyde* (2 g. in 25 c.c. of warm alcohol; hydrochloride, 2·3 g., in 20 c.c.; acetate, 1·4 g., in 20 c.c. of alcohol).—After being kept in cold water for an hour, the precipitate was collected and washed with water and with alcohol (yield 3·2 g.). N-p-*Nitrobenzyl-5-nitro-2-methoxybenzaldoxime* crystallises from nitrobenzene in yellow prisms, m. p. 237° (decomp.) (Found : N, 13·3. $C_{15}H_{13}O_6N_3$ requires N, 12·7%).

m-*Nitrobenzaldehyde* (0·37 g. in 5 c.c.; hydrochloride, 0·6 g., in 10 c.c.; acetate, 0·35 g., in 5 c.c.).—The reaction mixture was kept for 30 minutes and then diluted with water; an almost quantitative yield of *N*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime was obtained identical with that prepared from the sodium salt of the β-oxime. There was no indication of the formation of a second isomeride.

The System α-Benzaldoxime–p-*Nitrobenzyl Bromide.*

The α-benzaldoxime was crystallised from benzene and light petroleum; it melted in a capillary tube at 34° and froze in bulk at 32·9°. The *p*-nitrobenzyl bromide was crystallised first from light petroleum and then from alcohol; it melted in a capillary tube at 100° and froze in bulk at 97·9°. Cooling curves were constructed for mixtures of the two compounds in a vacuum-lagged silica vessel. It was found necessary to seed mixtures containing more than 87% of α-benzaldoxime with a crystal of α-benzaldoxime in order to induce crystallisation. The freezing points are given in Table III (*a* = molecular percentage of α-benzaldoxime).

TABLE III.

a.	F. p.	*a*.	F. p.	*a*.	F. p.	Eutectic.
0	97·9°	54·3	72·5°	85·6	37·8°	
4·3	96·1	61·1	67·7	88·9	27·8	27·2°
8·2	94·3	67·0	63·6	91·1	27·4	27·3
11·8	93·0	74·0	57·2	94·7	29·4	
18·1	89·2	78·1	51·7	97·3	30·8	
37·3	80·9	81·6	45·4	98·9	31·7	
47·2	76·5	83·6	41·2	100	32·9	

No indication of the formation of a compound was obtained. Equimolecular quantities of α-benzaldoxime and *p*-nitrobenzyl bromide dissolved in the minimum quantity of dry benzene were kept for 6 months. On removing the benzene, an oily solid was obtained which had the characteristic odour of α-benzaldoxime and, after being pressed on a porous tile, left a residue of *p*-nitrobenzyl bromide.

O-*Methyl Ethers of* m-*Nitrobenzaldoxime.*

Methoxyl Content and Molecular Weights.—The ethers employed were those prepared by Brady, Dunn, and Goldstein (J., 1926, 2398, 2402). α-*O*-Methyl-*m*-nitrobenzaldoxime has m. p. 63° (Found: OMe, 16·7; *M*, microcryoscopic in camphor, 181. Calc.: OMe, 17·2%; *M*, 180). β-*O*-Methyl-*m*-nitrobenzaldoxime has m. p. 75° (Found: OMe, 16·8%; *M*, microcryoscopic in camphor, 174).

Action of O-*Methylhydroxylamine on* m-*Nitrobenzaldehyde.*—The pure aldehyde (10 g.), dissolved in alcohol (150 c.c.), was mixed with *O*-methylhydroxylamine (3·3 g.) in alcohol (15 c.c.) and kept for 65 hours in a corked flask in the dark. The products were then precipitated in three fractions by very gradual addition of water with thorough stirring; in order to induce the third fraction to crystallise it was necessary to cool the mixture in ice. Fractions 1 and 2, constituting the bulk of the product (about 9 g.), were almost pure α-*O*-methyl-*m*-nitrobenzaldoxime (m. p. 63°). Fraction 3 (m. p. 42—44°) was redissolved in a small quantity of hot alcohol; from the cooled solution, more of the α-*O*-ether separated. The mother-liquor was cooled in ice and a little water added; a mixture then separated (m. p. 43—45°). After removal of this, further dilution followed by cooling in ice gave a product, m. p. 55—60°, which, after crystallisation from light petroleum, yielded a small quantity of nearly pure β-*O*-methyl-*m*-nitrobenzaldoxime, m. p. 70—71°; this melted at 73—74° and 45—50° when mixed with equal amounts of pure β-*O*-ether and α-*O*-ether, respectively. A similar result had previously been obtained by one of us using *O*-methylhydroxylamine hydrochloride, decomposed by sodium ethoxide in alcohol, and considerably smaller quantities of material.

Action of Ultra-violet Light on Some α-O-*Methyl Ethers.*

α-O-*Methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime.*—The ether was prepared by methylation of the oxime (Brady, Dunn, and Goldstein, *loc. cit.*). The same compound is formed when 6-nitro-3 : 4-methylenedioxybenzaldehyde (1 g.) in warm alcohol (40 c.c.) is mixed with a solution of *O*-methylhydroxylamine hydrochloride (0·5 g.) in a little water which has been treated with sodium ethoxide in alcohol (0·14 g. of sodium in 25 c.c. of alcohol); after a few hours crystals of the α-*O*-ether separate. The α-*O*-ether (2·5 g.), dissolved in benzene (100 c.c.), was exposed in a quartz flask to ultra-violet light for 72 hours. A small amount of brown, flocculent precipitate was removed, the solution evaporated, and the residue, m. p. 99—104°, dissolved in warm acetone (40 c.c.). The cold solution was then fractionally precipitated with water. The first fraction was the α-*O*-ether (m. p. 147°). The second and third fractions (m. p. 100—105°) were combined and crystallised four times from alcohol; 0·2 g. of β-O-*methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime* was then obtained in long, straw-coloured needles, m. p. 122° (Found: N, 12·7. $C_9H_8O_5N_2$ requires N, 12·5%). A mixture of approximately equal quantities of the α- and β-*O*-ethers melted at 107—108°. The β-*O*-ether, when dissolved in chloroform and treated for a few seconds with hydrogen chloride, is converted into the α-*O*-ether, the solution on evaporation giving a product which melts at 146°, and at 147° when mixed with α-*O*-ether.

α-O-*Methyl*-3-*nitro*-4-*methoxybenzaldoxime*.—Similar treatment of this compound resulted in partial inversion, but the product (m. p. 103—104°) could not be separated into its components. When it was dissolved in chloroform and treated with hydrogen chloride, and the solution was evaporated to dryness, the mixture was reconverted into the α-ether.

In conclusion, we wish to thank the Government Grant Committee of the Royal Society for a grant towards the cost of a quartz-mercury lamp.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February* 10*th*, 1927.]

CXXIX.—*The Isomerism of the Oximes. Part XXX. The Preparation of* o-*Methoxybenzaldoxime from Bisnitrosyl*-o-*methoxybenzyl.*

By OSCAR L. BRADY and CHARLES L. BENNETT.

THE preparation of the two isomeric forms of a substituted benzaldoxime is not always possible (Brady and Dunn, J., 1916, **109**, 666) and in no case is this more remarkable than in that of *o*-methoxybenzaldoxime, which exists only in the α-form, many attempts to obtain the isomeric β-compound through the hydrochloride in various ways, or by the action of light, having been completely unsuccessful (Brady and Dunn, J., 1923, **123**, 1787; Brady and McHugh, J., 1924, **125**, 584). For a summary of the facts bearing on this problem, see Brady, Cosson, and Roper (J., 1925, **127**, 2427). An attempt has now been made to prepare β-*o*-methoxybenzaldoxime by the method by which Behrend and Nissen (*Annalen*, 1892, **269**, 390) first obtained β-*o*-chlorobenzaldoxime (compare also Behrend and König, *Annalen*, 1891, **263**, 216, 348). The latter compound has now been prepared from the α-oxime by the action of ultra-violet light (Brady and McHugh, *loc. cit.*) and through the hydrochloride by a special method (Brady, Cosson, and Roper, *loc. cit.*), but at the time of Behrend and Nissen's work the hydrochloride method had not been successfully applied (Dollfus, *Ber.*, 1892, **25**, 1923).

The method involves the preparation of N-o-*methoxybenzyl*-p-*methoxybenzaldoxime* (I) from *o*-methoxybenzyl chloride and β-*p*-methoxybenzaldoxime, its hydrolysis to N-o-*methoxybenzylhydroxylamine hydrochloride* (II), the conversion of this into *nitroso*-N-o-*methoxybenzylhydroxylamine* (III), which with a trace of nitric acid yields *bisnitrosyl*-o-*methoxybenzyl* (IV); the last compound, on treatment with alkali, gives *o*-methoxybenzaldoxime.

$$(o)\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2Cl} + (p)\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CH{:}NOH} \longrightarrow$$

$$\text{(I.)}\ (p)\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CH{:}N({:}O){\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe}\ (o) \longrightarrow$$

$$\text{(II.)}\ (o)\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}OH,HCl} \longrightarrow$$

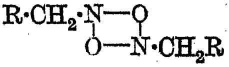
$$\text{(III.)}\ (o)\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}N(NO){\cdot}OH} \longrightarrow$$

$$\text{(IV.)}\ [(o)\ \mathrm{MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO}]_2 \longrightarrow \mathrm{MeO{\cdot}C_6H_4{\cdot}CH{:}NOH}$$

β-*p*-Methoxybenzaldoxime was chosen as the means of obtaining the *N*-ether, because this β-oxime is comparatively stable and is one of the easiest to prepare in the pure state. This method of obtaining the necessary *N*-substituted hydroxylamine was not used by Behrend and Nissen, but their method would have involved considerable loss of the valuable *o*-methoxybenzyl chloride.

Behrend and König, by decomposition of bisnitrosylbenzyl and of bisnitrosyl-*p*-nitrobenzyl, obtained approximately equal amounts of α- and β-benzaldoximes and α- and β-*p*-nitrobenzaldoximes, respectively, but it is difficult to say whether the α-oxime was a product of isomeric change of the β-oxime during the somewhat lengthy manipulations. If the structure of the bisnitrosyl compound adopted by Behrend be accepted (V) and the reaction be

(V.)



$$\begin{array}{l}\mathrm{R{\cdot}CH_2{\cdot}N{-}O}\\ \qquad\quad\ \mathrm{O{-}N{\cdot}CH_2R}\end{array}$$

regarded as a depolymerisation followed by tautomeric change of the nitrosobenzyl, the formation of a mixture of the two isomerides might be expected. Unfortunately, although there is considerable evidence that the decomposition of bisnitrosyl-*o*-methoxybenzyl leads to the formation of some β-methoxybenzaldoxime, it has not been possible to isolate enough of the β-oxime to identify it as thoroughly as could be desired.

EXPERIMENTAL.

N-o-*Methoxybenzyl*-p-*methoxybenzaldoxime* (I).—*o*-Methoxybenzyl chloride was prepared (1) by methylating saligenin with methyl iodide, methyl alcohol, and sodium methoxide, hydrolysing the product to *o*-methoxybenzyl alcohol, and converting this into the chloride with dry hydrogen chloride (Pschorr, Wolfes, and Buckow, *Ber.*, 1900, **33**, 165), (2) from *o*-methoxybenzaldehyde (from salicylaldehyde) by the Cannizzaro reaction.

A cold solution of β-*p*-methoxybenzaldoxime (10 g.) in the minimum quantity of absolute alcohol was treated with a cold solution of sodium (1·52 g.) in absolute alcohol and with an alcoholic solution of freshly distilled *o*-methoxybenzyl chloride (10 g.); a cloudiness appeared almost at once and heat was developed. After 12 hours, some of the *N*-ether had crystallised. Ice-cold water was added, and the crude *N*-ether separating was collected and dried over solid sodium hydroxide (yield, 95%). *o*-Methoxybenzyl chloride is readily hydrolysed by water, which must be excluded as completely as possible in the above preparation, otherwise the yield is much reduced. Crystallised from chloroform and light petroleum, N-o-*methoxybenzyl*-p-*methoxybenzaldoxime* formed colourless, monoclinic prisms, m. p. 123° (Found: N, 5·2. $C_{16}H_{17}O_3N$ requires N, 5·2%).

N-o-*Methoxybenzylhydroxylamine Hydrochloride* (II).—The crude *N*-ether obtained above was hydrolysed by boiling it under reflux for an hour with 20% hydrochloric acid; the *p*-methoxybenzaldehyde produced and any *O*-*o*-methoxybenzyl-*p*-methoxybenzaldoxime formed during methylation were then distilled in steam (*O*-ethers are not appreciably hydrolysed under these conditions). When the distillate no longer contained aldehyde, the hydrochloric acid solution remaining in the flask was evaporated on the water-bath until crystals appeared on the surface; on cooling, the greater part of the *N*-*o*-methoxybenzylhydroxylamine hydrochloride separated in crystals, usually tinged pink. Crystallised from absolute alcohol and dry ether, N-o-*methoxybenzylhydroxylamine hydrochloride* formed small, white needles, m. p. 136° (Found: N, 7·5; Cl, 18·6. $C_8H_{11}O_2N,HCl$ requires N, 7·4; Cl, 18·7%). It is a powerful reducing agent, acting upon ferric chloride and Fehling's solution immediately at room temperature.

Nitroso-N-o-*methoxybenzylhydroxylamine* (III).—A 3% aqueous solution of the above hydrochloride was cooled in ice, and an equivalent amount of sodium nitrite in the minimum amount of water added with stirring. After an hour the solution was thick with crystals, which were collected, washed with water, and air-dried (yield, 70%). Crystallised from chloroform and light petroleum, *nitroso*-N-o-*methoxybenzylhydroxylamine* was obtained in pale yellow, microscopic crystals, m. p. 73—74° (Found: N, 15·7. $C_8H_{10}O_3N_2$ requires N, 15·4%).

Bisnitrosyl-o-*methoxybenzyl* (IV).—*N*-*o*-Methoxybenzylhydroxylamine hydrochloride (5 g.) was dissolved in water (200 c.c.) and cooled in ice; a solution of hydrated sodium carbonate (4·2 g.) was added followed by glacial acetic acid (7·5 g.). Ether was poured on the mixture to form a layer, and an aqueous solution of potassium dichromate (2·66 g.) run in with vigorous stirring. After some time, the brown, flocculent, crystalline substance which had collected at the water–ether interface was removed, washed with a little ether, and dried (yield, 40—60%).

A much purer product was obtained by the following method. Nitroso-*N*-*o*-methoxybenzylhydroxylamine (5 g.) was dissolved in ether (60—70 c.c.), and glacial acetic acid (15 c.c.) was added together with one drop of fuming nitric acid. A steady stream of gas was evolved and after some time the sparingly soluble bisnitrosyl compound separated in 30—40% yield. After crystallising from chloroform and light petroleum, *bisnitrosyl*-o-*methoxybenzyl* was obtained in colourless needles, m. p. 125° (Found: N, 9·2. $C_{16}H_{18}O_4N_2$ requires N, 9·3%).

Action of Alkalis on Bisnitrosyl-o-*methoxybenzyl*.—Bisnitrosyl-*o*-methoxybenzyl was ground for some hours with 10% aqueous sodium hydroxide, cooling in ice. The undecomposed compound was filtered off, and a slight excess of an ice-cold, saturated solution of ammonium chloride added to the filtrate. The oxime, which was precipitated as an oil, was extracted with ether; on removal of the solvent, white crystals were obtained. These melted at 80—82°, and in admixture with α-*o*-methoxybenzaldoxime (m. p. 92°) at 59°. Under the microscope, they were seen to be a mixture of the characteristic long needles of the α-oxime and thin plates. Solution in alcohol and evaporation gave an oil which soon crystallised to the almost pure α-oxime, indicating that some unstable compound was present which changed rapidly to the α-oxime.

With 25% methyl-alcoholic potassium hydroxide, a more rapid decomposition of the bisnitrosyl compound occurred and the addition of ammonium chloride precipitated a compound, which melted alone at 80—85° and at 65° when mixed with the α-oxime. On crystallising it twice from acetone and water, a very small quantity of a product, m. p. 101—102°, was obtained as compact, white prisms distinct from the slender crystals of the α-oxime. This appeared to be the β-oxime. It was very unstable and when after a few days an attempt was made to determine its configuration it was found that the m. p. had fallen to 92° and that the compound then consisted of the pure α-oxime. In subsequent preparations, using various methods of alkaline decomposition, we were never successful in obtaining this high-melting product again, but the low-melting, crude oxime always gave an orange-red coloration with alcoholic ferric chloride—a reaction characteristic of the β-aldoximes (Beck and Hase, *Annalen*, 1907, **355**, 29) and not given by α-*o*-methoxybenzaldoxime. Moreover, treatment of the crude product with acetic anhydride and then with sodium carbonate solution, extraction with ether, and hydrolysis of the oily product with sodium hydroxide resulted in the evolution of some ammonia. This indicated the presence of nitrile, probably formed from β-oxime in the crude product. The hydrolysis product was saturated with carbon dioxide and extracted with ether; the ether on evaporation gave α-*o*-methoxybenzaldoxime. The aqueous solution was acidified with dilute sulphuric acid and again extracted with ether; *o*-methoxybenzoic acid was then obtained. The ratio of oxime to acid was approximately 4 to 1. The difficulty encountered in obtaining the β-oxime by this method seems to be due to the slowness of the decomposition of the bisnitrosyl compound; owing to the instability of the β-oxime, most of it probably changes to the α-isomeride during manipulation; and fractional crystallisation of the product provides still further opportunity for the isomerisation to occur.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February* 16*th*, 1927.]

CXXX.—*The Mechanism of the Reaction between a Carboxylic Ester and a Grignard Reagent.*

By DAVID RUNCIMAN BOYD and HAROLD HERBERT HATT.

FEW synthetic processes of organic chemistry have been more extensively used than that which leads to the formation of tertiary alcohols by the action of magnesium alkyl, or aryl, halides upon ethereal salts. The mechanism of the process, however, is still in some respects obscure. In his original papers dealing with this subject (*Compt. rend.*, 1901, **132**, 336; *Ann. Chim.*, 1901, **24**, 433), Grignard states that the reaction probably takes place in three stages:

(i) $R\cdot CO\cdot OEt \xrightarrow{R'\cdot MgBr} R\cdot CR'(OMgBr)\cdot OEt.$

(ii) $R\cdot CR'(OMgBr)\cdot OEt \xrightarrow{R'\cdot MgBr} R\cdot CR'_2\cdot OMgBr + EtO\cdot MgBr.$

(iii) $R\cdot CR'_2\cdot OMgBr \xrightarrow{H_2O} R\cdot CR'_2\cdot OH + HO\cdot MgBr.$

This scheme is reproduced in several well-known text-books.

An alternative view assumes that a ketone is formed as an intermediate product:

$$R\cdot CO\cdot OEt + R'\cdot MgBr = R\cdot CO\cdot R' + EtO\cdot MgBr;$$

and that the tertiary alcohol results from the action of the Grignard reagent upon the ketone. This mechanism was suggested by Reformatsky for the analogous case of an organo-zinc iodide reacting with an ethereal salt (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 881); it has been advocated by several writers, notably by Stadnikov (*Ber.*, 1914, **47**, 2133). Gomberg (*J. Amer. Chem. Soc.*, 1917, **39**, 2011) refers to Stadnikov's work as providing some evidence in support of the ketone hypothesis; but a consideration of Stadnikov's papers has led us to the conclusion that the evidence offered there is illusory.

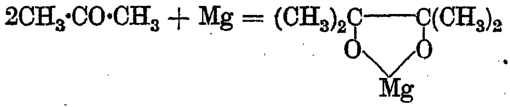
Ketones have, it is true, been obtained by Blaise and Courtot (*Compt. rend.*, 1905, **140**, 370) by the action of water on the addition compounds which are formed on treating the esters of certain unsaturated acids with magnesium methyl iodide at 0°, *e.g.*,

$$CH_2{:}C(CH_3)\cdot CO\cdot OEt \longrightarrow CH_3\cdot CH_2\cdot CH(CH_3)\cdot CO\cdot CH_3.$$

These results, however, are not out of harmony with Grignard's views. The appearance of a ketone amongst the products of the reaction may be attributed to the stability, under the conditions of the experiment, of the magnesium addition compound arising in stage (i) of the Grignard scheme. The experiments of Blaise and Courtot provide no evidence in support of the hypothesis that the formation of a ketone is a necessary step in the production of a tertiary alcohol. In order to establish the correctness of this view, it is necessary to show that the free ketone is present in the reaction mixture during the experiment. Such evidence we are now able to bring forward.

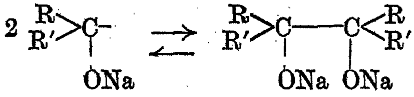
In connexion with investigations on derivatives of the triaryl carbinols, which have been in progress for some time, we have had frequent occasion to employ the Grignard reaction for the preparation of tertiary alcohols from ethereal salts, and in the course of this work we have found that if metallic magnesium is added to the reaction mixture the presence of a ketone is readily detected. When magnesium phenyl bromide, for example, was allowed to react with ethyl *o*-toluate in the presence of metallic magnesium, the products of the reaction included diphenyldi-*o*-tolylpinacol (38%) in addition to diphenyl-*o*-tolylcarbinol (23%). The addition of the Grignard reagent to the ester and magnesium was invariably followed by the development of a deep red colour, which persisted, provided air was excluded, until the reaction mixture was treated with water.

The formation of pinacols under the conditions described is easily understood in the light of the observations of Couturier and Meunier, who found (*Bull. Soc. chim.*, 1905, **33**, 454) that magnesium amalgam reacts smoothly with acetone, giving an addition compound from which the corresponding pinacol is obtained on treatment with water:



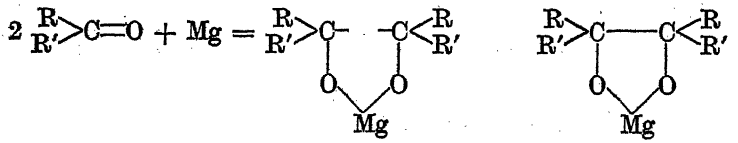
$$2CH_3\cdot CO\cdot CH_3 + Mg = \underset{O\diagdown\underset{Mg}{}\diagup O}{(CH_3)_2C\!-\!\!-\!\!-\!C(CH_3)_2}.$$

The more recent investigations of Schlenk (*Ber.*, 1911, **44**, 1182; 1913, **46**, 2840) have shown, further, that ketones combine with metallic sodium (or magnesium activated by iodine) to give intensely coloured metal ketyls, containing tervalent carbon, and that metallic pinacolates result from the union of two of these unsaturated molecules:



$$2\,{}^{R}_{R'}\!\!>\underset{ONa}{\overset{|}{C}}- \rightleftarrows {}^{R}_{R'}\!\!>\underset{ONa}{C}\!-\!\!-\!\underset{ONa}{C}\!<^{R}_{R'}$$

The phenomena observed in our experiments (production of pinacols and development of colour) are thus very simply explained if it is assumed that the ester reacts with the Grignard reagent to form a ketone and that some of the ketone escapes transformation to a tertiary alcohol by combining with metallic magnesium (activated by contact with the Grignard reagent):*



$$2\,{}^{R}_{R'}\!\!>C{=}O + Mg = {}^{R}_{R'}\!\!>\underset{O\diagdown Mg \diagup O}{C-\quad -C}\!<^{R}_{R'} \qquad {}^{R}_{R'}\!\!>\underset{O\diagdown Mg \diagup O}{C\!-\!\!-\!C}\!<^{R}_{R'}$$

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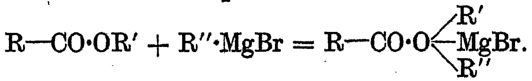
* Since this work was completed a paper has been published by Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 236) in which it is shown that ketones are converted into pinacols by magnesium in the presence of a Grignard reagent or, more effectively, by treating the ketone with a mixture of magnesium and magnesium iodide. The activation of the magnesium in

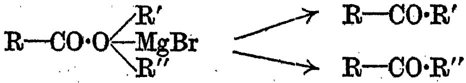
Grignard's scheme, on the other hand, cannot be reconciled with the observed phenomena and must therefore be rejected in favour of the ketone hypothesis.

There remains the question, By what mechanism is the ketone produced from the ester? On theoretical grounds, it appears probable that the Grignard reagent and the ethereal salt react in the first place to give an additive compound, and that the ketone results from the decomposition of this primary complex. Some experimental evidence in support of this view is on record. Stadnikov (*loc. cit.*) found that benzhydryl acetate reacts, in the cold, with magnesium ethyl iodide to give an addition compound, from which the original ester can be recovered on treatment with water. Addition compounds of a somewhat similar character have been obtained from certain ketones (compare Klages, *Ber.*, 1902, **35**, 2633). Stadnikov explains his observations by postulating the formation of an oxonium compound:



$$R{-}CO{\cdot}OR' + R''{\cdot}MgBr = R{-}CO{\cdot}O\begin{cases}R'\\MgBr.\\R''\end{cases}$$

The groups R′ and R″ in this complex are assumed by Stadnikov to be similarly situated, and the conclusion is drawn that two different ketones may result from its decomposition:



$$R{-}CO{\cdot}O\begin{cases}R'\\MgBr\\R''\end{cases}\begin{matrix}\nearrow R{-}CO{\cdot}R'\\ \searrow R{-}CO{\cdot}R''\end{matrix}$$

Stadnikov claims to have obtained experimental proof of the correctness of this hypothesis from the results of a study of the action of magnesium phenyl bromide upon (*a*) benzyl benzoate and (*b*) benzhydryl acetate.

The principal product of reaction (*a*) is triphenylcarbinol; but, in addition to this, Stadnikov isolated a small quantity of a substance, m. p. 72—73°, which he assumed to be triphenylethylene.

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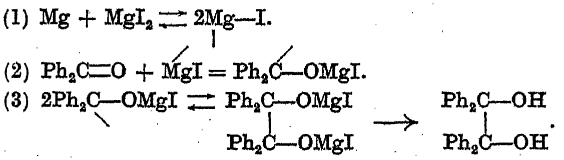
both cases is attributed by Gomberg and Bachmann to the formation of a magnesous iodide:



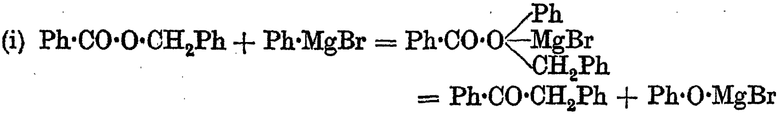
$$(1)\ Mg + MgI_2 \rightleftharpoons 2\overset{|}{Mg}{-}I.$$

$$(2)\ Ph_2C{=}O + \overset{/}{M}gI = Ph_2\overset{/}{C}{-}OMgI.$$

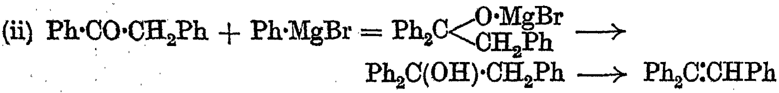
$$(3)\ 2Ph_2\underset{\diagdown}{C}{-}OMgI \rightleftharpoons \begin{matrix}Ph_2C{-}OMgI\\|\\Ph_2C{-}OMgI\end{matrix} \longrightarrow \begin{matrix}Ph_2C{-}OH\\|\\Ph_2C{-}OH\end{matrix}$$

Very large yields of pinacols (92—99·6%) were obtained from eight ketones by Gomberg and Bachmann; and these authors have proved that the *simultaneous* action of both magnesium and magnesium iodide is demanded in the reduction of ketones.

On this assumption, he argues that phenyl benzyl ketone must have been formed as an intermediate product:



$$\text{(i) } \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CH_2Ph + Ph{\cdot}MgBr = Ph{\cdot}CO{\cdot}O} \lt \begin{matrix} \mathrm{Ph} \\ \mathrm{MgBr} \\ \mathrm{CH_2Ph} \end{matrix}$$
$$= \mathrm{Ph{\cdot}CO{\cdot}CH_2Ph + Ph{\cdot}O{\cdot}MgBr}$$

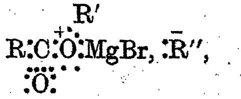


$$\text{(ii) } \mathrm{Ph{\cdot}CO{\cdot}CH_2Ph + Ph{\cdot}MgBr = Ph_2C} \lt \begin{matrix} \mathrm{O{\cdot}MgBr} \\ \mathrm{CH_2Ph} \end{matrix} \longrightarrow$$
$$\mathrm{Ph_2C(OH){\cdot}CH_2Ph} \longrightarrow \mathrm{Ph_2C{:}CHPh}$$

No evidence is given in support of the formula $Ph_2C{:}CHPh$ except the analytical data: C, 93·34; H, 6·64%. These figures, however, are in excellent agreement with the composition of diphenyl (C, 93·46; H, 6·54%). The melting point given for the supposed triphenylethylene is the same as that of diphenyl, and the description of the crystalline form and solubility agrees with the assumption that the compound was diphenyl. On repeating Stadnikov's experiment we obtained the substance he describes, and identified it as diphenyl by the melting point of a mixture with an authentic specimen and by conversion into the dibromide.

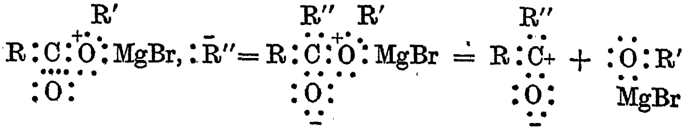
Amongst the products of reaction (*b*), Stadnikov obtained a hydrocarbon, m. p. 121—122°, which he assumed to be methyltriphenylethylene. The formation of the compound is explained as due to a series of changes similar to those given for case (*a*), and involving the production of benzhydryl methyl ketone as an intermediate step. Again, no evidence is brought forward in proof of the formula $CPh(CH_3){:}CPh_2$, except the analytical data. The figures given agree equally well with the compositions of several other substances,. Methyltriphenylethylene has recently been prepared by methods which leave no doubt as to its constitution (Levy, *Bull. Soc. chim.*, 1921, 29, 890); it melts at 89—90°.

There is thus no experimental foundation for the view that an ester, $R{\cdot}CO{\cdot}OR'$, can react with a Grignard reagent, $R''{\cdot}MgBr$, to give a ketone with the formula $R{\cdot}CO{\cdot}R'$. Hence Stadnikov's oxonium formula, in its original form, must be rejected, since it suggests possibilities of reaction which are not realised in practice. If, however, the Stadnikov formula is written in electronic fashion,



$$R{:}\underset{:\ddot{O}:}{C}{:}\overset{R'}{\overset{+\,\cdot\cdot}{O}}{:}MgBr,\ {:}\overset{-}{R}'',$$

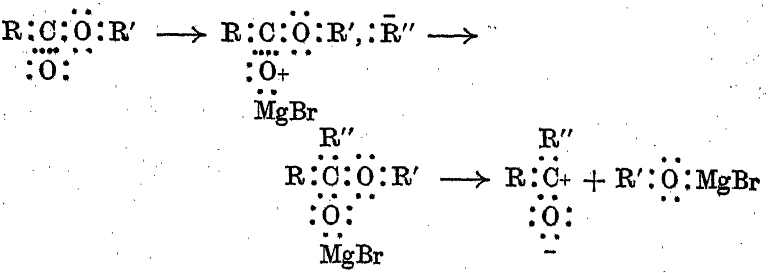
it becomes apparent that the groups R′ and R″ are not similarly situated. R″ is negatively charged and retained in the molecule by the electrostatic attraction of the positive oxonium oxygen atom; R′, on the other hand, is attached by a co-valency to the oxygen. The rearrangement of the oxonium compound will naturally take place by a movement of the radical R″, the radical R′ retaining its original position. Hence only one ketone will be formed.



$$R:\underset{:O:}{C}:\overset{R'}{\overset{+}{O}}:MgBr,\ :\bar{R}'' = R:\underset{:\underset{-}{O}:}{\overset{R''}{C}}:\overset{R'}{\overset{+}{O}}:MgBr \rightleftharpoons R:\underset{:\underset{-}{O}:}{\overset{R''}{C}}{}^{+} + :\underset{MgBr}{O}:R'$$

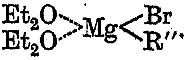
(I.) (II.)

The magnesium complex (II) may be expected to break down with extreme ease, giving free ketone and the aryloxy-magnesium halide. The ketone thus liberated will be in a highly reactive form, and rapid combination with a Grignard reagent, or with activated magnesium, may be anticipated. This hypothesis appears to us to be the most satisfactory way of interpreting the phenomena. It is possible, however, that the formation of the primary addition compound may be due to the residual affinity of the carbonyl oxygen (compare v. Braun and Kirschbaum, *Ber.*, 1919, 52, 1725, for the analogous case of a ketone addition compound), and not to that of the ethereal oxygen :



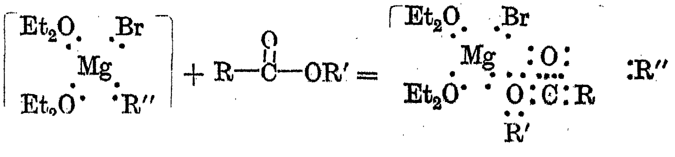
$$R:\underset{:O:}{C}:O:R' \longrightarrow R:\underset{:\underset{MgBr}{O^{+}}}{C}:O:R',\ :\bar{R}'' \longrightarrow$$
$$R:\underset{:\underset{MgBr}{O}:}{\overset{R''}{C}}:O:R' \longrightarrow R:\underset{:\underset{-}{O}:}{\overset{R''}{C}}{}^{+} + R':O:MgBr$$

Either view can be combined with the interesting suggestions of Meisenheimer and Casper (*Ber.*, 1921, 54, 1655), who regard the Grignard reagent as a magnesium complex compound containing two molecules of ether,



$$\begin{matrix}Et_2O\\ Et_2O\end{matrix}>Mg<\begin{matrix}Br\\ R''.\end{matrix}$$

The primary reaction between this compound and an ethereal salt may be represented as follows :



$$\left[\begin{matrix}Et_2O\cdot & & \cdot Br\\ & Mg & \\ Et_2O\cdot & & \cdot R''\end{matrix}\right] + R-\overset{O}{\overset{\|}{C}}-OR' = \left[\begin{matrix}Et_2O\cdot & & \cdot Br & \\ & Mg & & :O: \\ Et_2O\cdot & & \cdot O: & C:R \\ & & R' & \end{matrix}\right. \quad :R''$$

Considered as a practical method for the preparation of pinacols, the new process presents advantages in certain cases, since it starts from the ester, which is usually more accessible than the ketone. Indirectly it provides a method for the synthesis of ketones and secondary alcohols, pinacols being readily decomposed into these products. The yield of pinacol, however, varies greatly in different cases. It appears to be dependent upon the constitutions of both the ester and the Grignard reagent: the study of the reaction from this point of view is being continued.

One other point of some practical importance may be noticed. In the preparation of triphenylcarbinol from magnesium phenyl bromide the crude carbinol is always associated with other compounds which lower its melting point and render its isolation in good yield less easy than might be expected. One of these compounds, diphenyl (invariably formed during the preparation of the Grignard reagent), is well known and easily removed. But the literature contains references to other by-products whose constitutions have not been elucidated. Schroeter, in an experiment on the preparation of triphenylcarbinol from carbon dioxide and magnesium phenyl bromide (*Ber.*, 1903, **36**, 3005), obtained a substance (A), m. p. 165°, which he suggests may be a molecular compound of triphenylcarbinol with benzophenone; and also a small quantity of a substance (B), m. p. 81°. From the description given of the properties of (A) there can be little doubt that it was an impure specimen of benzpinacol. As to the constitution of (B), Schroeter offers no opinion. A compound melting at about the same temperature (83—84°) was recently obtained by Stadnikov (*Ber.*, 1924, **57**, 1)] from methyl benzoate by prolonged boiling with a Grignard reagent prepared from bromobenzene. This compound was regarded by Stadnikov as the methyl ether of triphenylcarbinol, and an elaborate series of equations is given to account for its formation. We have repeated Stadnikov's experiment several times and have also tried various modifications of the conditions, but on no occasion have we detected the presence of the methyl ether of triphenylcarbinol amongst the products of the reaction between methyl benzoate and magnesium phenyl bromide.

We have, however, observed the occurrence of a small quantity of the *ethyl* ether of triphenylcarbinol as a by-product in the preparation of the carbinol from methyl benzoate and magnesium phenyl bromide in certain cases when ethyl alcohol was used as the crystallisation medium.

The methyl and ethyl ethers of triphenylcarbinol may easily be confused; their melting points do not differ by more than a degree (m. p. of methyl ether, 82°; m. p. of ethyl ether, 83°. Richter's

Lexikon), and their percentage compositions are almost identical. They can readily be distinguished by a mixed melting point determination, but Stadnikov makes no mention of such an observation. In the circumstances, we are of opinion that the compound, m. p. 83—84°, obtained by him from methyl benzoate was the ethyl ether of triphenylcarbinol and not, as he supposed, the methyl compound. Schroeter's substance, m. p. 81°, was, doubtless, also the ethyl ether of the carbinol.

EXPERIMENTAL.

In the preparation of the Grignard reagents, iodine was employed in small quantity to activate the magnesium.

The Action of Magnesium Phenyl Bromide on Ethyl o-*Toluate.*— Bistrzycki and Gyr (*Ber.*, 1904, **37**, 1248) obtained a 40% yield of diphenyl-*o*-tolylcarbinol from methyl *o*-toluate and magnesium phenyl bromide; they do not record the formation of any by-products. In our experiments, the ethyl ester was used.

Expt. 1. The product obtained on decomposing the magnesium complex with ice and dilute sulphuric acid was steam-distilled, and the residue crystallised from light petroleum and alcohol. The yield of carbinol, m. p. 98—98·5°, was 28·5%.

Expt. 2. 41 G. of the ester, dissolved in 60 c.c. of ether, were added to a Grignard reagent prepared from 13·5 g. of magnesium, 98 g. of bromobenzene and 200 c.c. of ether. In the hope of improving the yield, the procedure was modified as follows. After decomposition of the magnesium compound, the ethereal layer was removed, and the ether distilled off. On pouring the residual oil into alcohol, fine, white needles (A), m. p. 155°, immediately separated. Further small quantities of (A) were deposited from the solution on keeping, the total yield being 6·7 g. The residue left on evaporation of the alcoholic solution was steam-distilled, and the non-volatile portion crystallised from alcohol. In this way, 20·3 g. of diphenyl-*o*-tolylcarbinol were obtained. From the oil remaining after this crystallisation, 7·35 g. of diphenyl-*o*-tolylchloromethane were precipitated on passing hydrogen chloride gas through an ethereal solution containing fused calcium chloride.

The product (A), after several crystallisations from aqueous alcohol, melted at 160°. It crystallised well from benzene (needles, rapidly efflorescing in the air), or glacial acetic acid. It was identified as *diphenyldi-*o*-tolylpinacol* by analysis (C, 85·1; H, 6·9. $C_{28}H_{26}O_2$ requires C, 85·2; H, 6·65%) and by conversion into a mixture of phenyl-*o*-tolylcarbinol and phenyl *o*-tolyl ketone. Transformation into the secondary alcohol and ketone was brought about either by heating for some hours at 120—125° or by treatment with hot alcoholic potash. On treatment with this reagent, it dissolved, imparting a characteristic, fleeting, deep-blue colour to the solution (compare Schlenk and Thal, *Ber.*, 1913, **46**, 2840). The oily product of the reaction, on being rubbed with light petroleum, gave crystals of phenyl-*o*-tolylcarbinol, identified by melting point (91·5°, after three crystallisations from ether–light petroleum) and by analysis (C, 84·9; H, 7·3. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). The oil left after separation of the phenyl-*o*-tolylcarbinol boiled at 286—288°, and on treatment with alkaline-alcoholic hydroxylamine gave an oxime, m. p. 101·5—103·5° after crystallisation from aqueous alcohol. Smith (*Ber.*, 1891, **24**, 4046) gives 105° as the melting point of *anti*-phenyl-*o*-tolylketoxime.

The yields of pinacol and carbinol in this experiment were, respectively, 13·6% and 39·7%. Cohen, who prepared diphenyldi-*o*-tolylpinacol by reduction of phenyl *o*-tolyl ketone (*Rec. trav. chim.*, 1919, **38**, 113), gives 163° as the melting point.

Expt. 3. The formation of pinacol in the preceding experiment was attributed to the presence in the reaction mixture of some metallic magnesium left over in the preparation of the Grignard reagent. This view was confirmed by removing any undissolved metal as completely as possible before allowing the reagent to mix with the ester. For this purpose, the Grignard reagent was filtered through an asbestos pad before entering the solution of ester (7·5 g.) in dry ether. The reaction product, after treatment in the usual way, was poured into alcohol, kept for 9 days, and inoculated with diphenyldi-*o*-tolylpinacol; 0·02 g. of product, m. p. 154°, was then obtained (equivalent to a yield of 0·26% of pinacol). On addition of light petroleum to the oily liquid, from which the pinacol had separated, diphenyl-*o*-tolylcarbinol (1·29 g.) crystallised; and the mother-liquor from this crystallisation, on long standing, deposited 0·77 g. of the *ethyl ether* of diphenyl-*o*-tolylcarbinol (large, colourless prisms, m. p. 96°), identified by the melting point of a mixture with a specimen prepared from diphenyl-*o*-tolylcarbinyl chloride (Found: OEt, 11·56. $C_{20}H_{17}OEt$ requires OEt, 14·9%).

Expt. 4. In order to obtain a maximum yield of pinacol, the reaction was carried out in the presence of a considerable excess of magnesium. The Grignard reagent, prepared from 16·2 g. of bromobenzene, 5 g. of magnesium, and 50 c.c. of dry ether, was filtered from the excess of magnesium, and the excess of metal was introduced into a solution of 7·5 g. of ethyl *o*-toluate in 30 c.c. of dry ether. The Grignard reagent was then added gradually (3 hours) to the ester solution, which was stirred and refluxed gently. Heating was continued for an hour after all the reagent had been added. All these operations were carried out in an atmosphere of dry nitrogen. The reaction mixture remained throughout a deep red-orange colour. The product, treated in the usual way, gave 3·62 g. of pinacol (38%) and 2·92 g. of carbinol (23·3%).

The Action of Magnesium Phenyl Bromide on Methyl Benzoate.—In the following experiments, no attempt was made to exclude dry atmospheric oxygen.

Expt. 1. A Grignard reagent (prepared from 24·4 g. of bromobenzene, 7·5 g. of magnesium, and 70 c.c. of ether) was mixed with an ethereal solution of 20·9 g. of methyl benzoate, to which had been added the magnesium remaining over in the preparation of the magnesium phenyl bromide. The product was decomposed with ice and dilute sulphuric acid and extracted with ether. The semi-crystalline mass left on evaporation of the ether gave, on fractional crystallisation from ethyl alcohol, 8·7 g. (43·5%) of triphenylcarbinol (m. p. 160—161°) and 0·6 g. (2·2%) of benzpinacol, melting at 166—167° (m. p. after two crystallisations from aqueous alcohol, 185—186°). The benzpinacol was identified by conversion into benzhydrol (m. p. 67°) and benzophenoneoxime (m. p. 142—143°). The oil which did not crystallise in this treatment was steam-distilled. The steam distillate on fractional distillation yielded 10·08 g. of methyl benzoate, 0·3 g. of diphenyl, and 1·12 g. of residue. From the 1·12 g. of residue there resulted, on treatment with alkaline-alcoholic hydroxylamine, 0·46 g. of benzophenoneoxime, m. p. 142—143° after two crystallisations from aqueous alcohol (mixed m. p. 142—143°). The oil remaining after the steam distillation amounted to 2·55 g., and this when fractionally crystallised yielded, besides triphenylcarbinol, some colourless crystals melting between 70° and 78°. These, on recrystallisation from methyl alcohol, melted at 81—82°; they were identified as the ethyl ether of triphenylcarbinol. Mixed with a specimen of this ether (m. p. 80—82°), the crystals melted at 81·5°. A mixture of the substance with the methyl ether of triphenylcarbinol (m. p. 83—84°) melted at 60—63°, softening at 58°. A mixture of the methyl and ethyl ethers of triphenylcarbinol melted at 66—70°, softening at 53°.

Expt. 2. The Grignard reagent (prepared from 24·1 g. of bromobenzene, 4·5 g. of magnesium, and 70 c.c. of ether) was filtered and added slowly to an ethereal solution of 20·9 g. of methyl benzoate, containing 2·5 g. of magnesium turnings and a little metallic mercury. The reaction product, worked up in the usual way, yielded 2·15 g. (7·8%) of benzpinacol and 8·3 g. (41·5%) of triphenylcarbinol.

Expt. 3. Methyl benzoate (14 g.) was added fairly rapidly to a

Grignard reagent prepared from 34 g. of bromobenzene, 4·8 g. of magnesium, and 100 c.c. of ether. After the first reaction had ceased, the mixture was refluxed in a water-bath for 15 hours. The product was worked up as in Expt. 1, but the ethereal solution before evaporation was shaken with dilute aqueous sodium hydroxide in order to remove any free sulphuric acid. The following yields were obtained: triphenylcarbinol, 13·3 g. (49·7%); benzpinacol, 0·11 g.; and the ethyl ether of triphenylcarbinol, 1·62 g. (5·7%). The last compound was identified by a mixed melting point (83°), and conversion into the carbinol (mixed m. p. 160—161°) by treatment with concentrated sulphuric acid and glacial acetic acid.

The Action of Magnesium o-*Tolyl Bromide on Ethyl* o-*Toluate*.—The reaction was carried out exactly as described under Expt. 4 for the preparation of diphenyldi-*o*-tolylpinacol. The Grignard reagent was prepared from 16·5 g. of *o*-bromotoluene, 4·6 g. of magnesium, and 50 c.c. of ether; the undissolved magnesium being transferred to the solution of ethyl *o*-toluate (6·7 g.) in 30 c.c. of ether.

Immediately the Grignard reagent entered the ester solution, a deep reddish-violet colour was observed, which persisted until treatment of the reaction products with ice and dilute sulphuric acid. The ethereal layer on evaporation left an oil. From this residual oil, after rubbing with alcohol, a crystalline powder separated, m. p. 158° (yield 0·46 g.); and, on keeping, a further 0·02 g. of crystals (m. p. 148—153°) was obtained. This substance was very soluble in hot benzene, moderately easily soluble in alcohol, and insoluble in light petroleum. It was analysed after recrystallisation from benzene (Found: C, 85·2; H, 7·25. Calc. for $C_{30}H_{30}O_2$: C, 85·3; H, 7·2%). From its analysis, its decomposition on melting, and the evanescent deep green colour which it gives on dissolving in hot alcoholic sodium ethoxide, the substance is evidently *tetra*-o-*tolylpinacol*. The yield of pinacol was 5·2%.

The oil left after crystallisation of the pinacol was steam-distilled. From the distillate, 0·2 g. of a crystalline substance was obtained, melting, after crystallisation from aqueous alcohol, at 118—122°. The residue from the steam distillation was extracted with ether, and the ethereal solution was dried and evaporated. An oil was thus obtained which, on being rubbed with light petroleum containing a little ether, gave 0·51 g. of the same crystalline substance. After crystallisation from aqueous alcohol, it melted at 119—119·5°. A mixed melting-point determination showed that it was not di-*p*-tolyl. Analysis after recrystallisation pointed to *di*-o-*tolylcarbinol* (Found: C, 84·7; H, 7·7. $C_{15}H_{16}O$ requires C, 84·9;

H, 7·6%). The substance dissolved in concentrated sulphuric acid, giving a strong red colour. The di-*o*-tolylcarbinol may arise from hydrolysis of the pinacol by magnesium hydroxide during the decomposition of the reaction products with ice. Tri-*o*-tolylcarbinol has not, so far, been isolated, and the study of this reaction is being continued.

The Action of Magnesium Phenyl Bromide on Benzyl Benzoate (Stadnikov, *Ber.*, 1914, 47, 2140).—Benzyl benzoate was prepared from benzoyl chloride and benzyl alcohol by a Schotten–Baumann reaction. It was purified by fractionating it twice under reduced pressure. The ester was brought into reaction with magnesium phenyl bromide, the same amounts of reagents and the same procedure being used as directed by Stadnikov (*loc. cit.*). In the main, the products of the reaction were those recorded by Stadnikov; thus we obtained 0·25 g. of benzoic acid and 29·1 g. of triphenylcarbinol. The steam distillate was separated into two fractions, as he directs, and from the first there were obtained 5·9 g. of bromobenzene (b. p. 146—147°), 6·8 g. of benzyl alcohol (b. p. 201—205°), and a small amount of a crystalline residue. From the second fraction, 6 g. of benzyl alcohol (b. p. 204—210°) were obtained, together with 0·89 g. of the crystalline material supposed to be triphenylethylene. This substance melted at 62—67°, and, after two crystallisations from aqueous ethyl alcohol, formed colourless plates, m. p. 70—71°. The yield of pure product was 0·57 g. (Stadnikov obtained 0·55 g.). Mixed with diphenyl (m. p. 69—69·5°), the substance melted at 69·5—70·5°.

It was brominated by dissolving 0·5 g. in 3 g. of carbon disulphide and adding 3 g. of bromine. After refluxing for 6 hours, the carbon disulphide was evaporated under reduced pressure, and the crystalline product washed with caustic soda solution, water, and alcohol (yield, 0·72 g.). After two crystallisations from benzene, it formed small, colourless needles, m. p. 164·5°.

4 : 4′-Dibromodiphenyl, prepared in precisely the same manner from 0·5 g. of diphenyl and crystallised twice from benzene, melted at 163—164°. For the mixed melting point, the value 163·5—164·5° was obtained.

Postscript.—Barnett, Cook, and Nixon (this vol., p. 504) have recorded the formation of *s*-*oo*′-dibenzylbenzpinacol as one of the products of the action of magnesium phenyl bromide on ethyl *o*-benzylbenzoate. The announcement of our results led these authors to repeat this experiment, and in a private communication they inform us that, in agreement with our observations, they obtained no pinacol when a filtered solution of magnesium phenyl bromide was employed.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us (H. H. H.) to take part in this investigation.

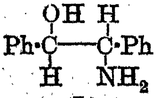
UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, February 12th*, 1927.]

CXXXI.—*The Optically Active Diphenylhydroxyethylamines and* iso*Hydrobenzoins. Part I.*

By JOHN READ and CATHERINE CASSELS STEELE.

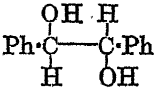
THE constitution, OH·CHPh·CHPh·NH_2, assigned to the diphenylhydroxyethylamines contains two dissimilar asymmetric carbon atoms and thus demands two externally compensated and four optically active stereoisomerides. A mixture of the two externally compensated bases is produced (i) in the reduction of benzoinoxime with sodium amalgam (Söderbaum, *Ber.*, 1895, **28**, 2523), and (ii) in the condensation of benzaldehyde and glycine (Erlenmeyer, *Annalen*, 1899, **307**, 97), diphenylhydroxyethylamine (m. p. 163°) predominating in the first reaction and *iso*diphenylhydroxyethylamine (m. p. 129—130°) in the second. Only the *iso*-base appears to have been resolved into optically active components (*Annalen*, 1904, **337**, 321; compare *Ber.*, 1899, **32**, 2378).

The base of m. p. 129—130° was originally regarded as *iso*diphenylhydroxyethylamine (I) by Erlenmeyer (*Annalen*, 1899, **307**, 97) because of its conversion by nitrous acid into *iso*hydrobenzoin; the latter substance, owing to its resolution into optically active components (*vide infra*), was assigned configuration (II). According to this scheme, diphenylhydroxyethylamine (m. p. 163°) would correspond configurationally to internally compensated hydrobenzoin (IV), thus possessing configuration (III):



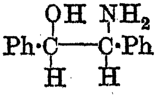
$$\mathrm{Ph{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\text{—}\underset{\mathrm{NH_2}}{\overset{\mathrm{H}}{\mathrm{C}}}\mathrm{{\cdot}Ph}$$

(I.)



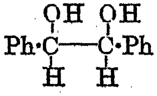
$$\mathrm{Ph{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\text{—}\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\mathrm{{\cdot}Ph}$$

(II.)



$$\mathrm{Ph{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\text{—}\underset{\mathrm{H}}{\overset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{{\cdot}Ph}$$

(III.)



$$\mathrm{Ph{\cdot}}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\text{—}\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\mathrm{{\cdot}Ph}$$

(IV.)

It was found later, however, that both of the externally compensated bases gave a mixture of *iso*hydrobenzoin and hydrobenzoin in this reaction, the former product predominating in each instance (*Annalen*, 1899, **307**, 130, 136). Erlenmeyer was in consequence led to postulate the intermediate formation of a diazo-compound, Ph·CH(OH)·C(:N_2)·Ph, containing only one asymmetric carbon atom in the molecule. The mechanism of the reaction has been discussed more recently by McKenzie and Richardson (J., 1923, **123**, 82).

We now describe the optical resolution of *dl*-diphenylhydroxyethylamine with *d*-oxymethylenecamphor and also with *d*-camphorsulphonic acid; the base appears to form a partly racemic salt with *d*-α-bromocamphorsulphonic acid. The optical rotatory powers of the two stereoisomeric bases show some remarkable contrasts: the respective values of $[\alpha]_D$ for *d*-diphenylhydroxyethylamine, *d*-diphenylhydroxyethylamine hydrochloride, and benzylidene-*d*-diphenylhydroxyethylamine were + 10·0° (alcohol), + 69·3° (water), and − 81·4° (alcohol); the corresponding values observed by us for the *d*-*iso*-base and its hydrochloride were + 125·0° and + 81·7°, whilst benzylidene-*d*-*iso*diphenylhydroxyethylamine gave $[\alpha]_D$ + 56·0° (*Annalen*, 1904, **337**, 343). *d*-Diphenylhydroxyethylamine showed a strong mutarotation in acetone, $[\alpha]_D$ changing from + 15·1° to − 108·8° in 90 minutes; the corresponding change for the *l*-*iso*-base was from − 102·2° to − 90·3°; in this respect, the *iso*-base thus appears to provide the closer analogy to the constitutionally similar hydroxyhydrindamine, the optically active forms of which show a weak but distinct mutarotation in acetone (J., 1912, **101**, 769).

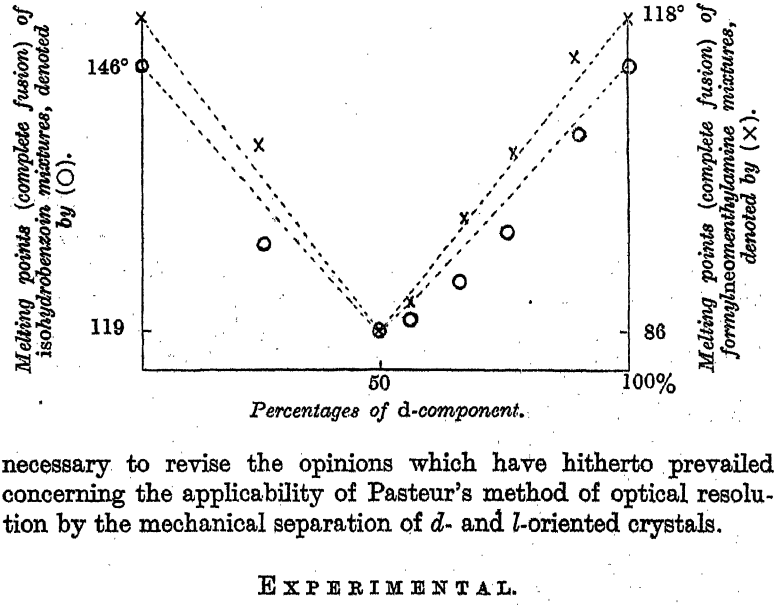
Upon treatment with nitrous acid, *dl*-diphenylhydroxyethylamine gave a mixture containing hydrobenzoin, *dl*-*iso*hydrobenzoin, and probably deoxybenzoin; the crude products obtained similarly from *l*-diphenylhydroxyethylamine, *l*-*iso*diphenylhydroxyethylamine and *d*-*iso*diphenylhydroxyethylamine had $[\alpha]_D$ + 38·9°, − 47·1°, and + 49·7°, respectively, in alcohol. When fractionally crystallised, these optically active preparations yielded pure *d*- or *l*-*iso*-hydrobenzoin, having m. p. 146° and $[\alpha]_D$ ± 90° approximately. The broad quantitative resemblance between the rotatory powers of the three crude products accords with Erlenmeyer's suggestion of the intermediate formation of a diazo-compound, but the results may be held alternatively to denote the occurrence of a Walden inversion affecting the enantiomorphously disposed groups $\cdot CH(NH_2)Ph$ of formulæ (I) and (III), the same equilibrium being reached from the two sides. The oily material formed in the reactions may contain diphenylacetaldehyde, produced as a result of concomitant semipinacolinic deamination (compare McKenzie and Roger, J., 1924, **125**, 844). Since *l*-diphenylhydroxyethylamine and *d*-*iso*diphenylhydroxyethylamine both yield *d*-*iso*hydrobenzoin, it may be inferred that the group $Ph\cdot CH(OH)\cdot$ has a similar spatial disposition in the molecules of these two bases: for example, if formula (I) is *d*-*iso*diphenylhydroxyethylamine, (III) is *l*-diphenylhydroxyethylamine. It appears that the optically active *iso*hydrobenzoins are less soluble than either *dl*-*iso*hydrobenzoin or hydrobenzoin.

The reaction with nitrous acid thus affords no decisive evidence concerning the molecular configurations of the stereoisomeric bases. We suggest, however, that diphenylhydroxyethylamine probably possesses the more symmetric configuration (III), on account of (*a*) the low rotatory power of the free base, (*b*) the remarkable change in rotatory power upon annulling the electropositive influence of the amino-group, and (*c*) the comparative ease with which this base yields condensation products containing heterocyclic ring-systems (compare *Ber.*, 1896, **29**, 1210; *Annalen*, 1904, **337**, 352). The *iso*-base would thus correspond to configuration (I), as suggested by Erlenmeyer on grounds which are no longer tenable (*vide supra*).

Bodewig (*Annalen*, 1876, **182**, 279) found that the crystals separating from ethereal solutions of optically inactive *iso*hydrobenzoin were hemihedral, and by means of a mechanical separation of *d*- and *l*-crystals Erlenmeyer (*Ber.*, 1897, **30**, 1531) obtained specimens exhibiting optical activity in alcoholic solution. The polarimetric data are not precise, and no melting points are quoted, but apparently the maximum rotation observed was $[\alpha]_D - 7{\cdot}30°$. Since we now record maximum values of $[\alpha]_D + 90{\cdot}5°$ and $- 89{\cdot}7°$ for *d*- and *l*-*iso*hydrobenzoin, respectively, it appears that the selected crystals contained not more than 54% of the *l*-component. The fission of *dl*-*iso*hydrobenzoin into optically active components by Erlenmeyer has been accepted for thirty years as a standard example of optical resolution by Pasteur's first method of so-called " spontaneous separation of enantiomers " (compare A. Werner, " Lehrbuch der Stereochemie," 1904, p. 62). It now appears that the formation of well-defined enantiomorphous crystals is not necessarily indicative of a complete optical resolution by this method. The melting-point curve of mixtures of *d*- and *l*-*iso*hydrobenzoin (Fig. 1) departs so markedly from the rectilinear form, when the temperatures of complete fusion are plotted, as to be incompatible with the existence of a conglomerate; the curve conforms, in fact, to Roozeboom's Fig. 11 (*Z. physikal. Chem.*, 1899, **28**, 510), thus indicating the formation of mixed crystals.

It is thus shown that mixed crystals derived from externally compensated organic substances may crystallise in enantiomorphously developed forms. In the light of these observations, it now seems justifiable to advance formyl-*dl*-*neo*menthylamine as a second example of the kind. This substance also yields *d*- and *l*-oriented crystals with hemihedral facets, which, again, display only a slight optical activity in solution; whilst pure formyl-*d*-*neo*menthylamine exhibits no hemihedry (J., 1926, 2228, 2219). Although in this case the melting-point curve (Fig. 1) does not depart so markedly from the conglomerate type as the above-mentioned curve, yet a certain similarity to Roozeboom's Fig. 11 is manifest; moreover, it is clear that a crystal containing a slight excess of one enantiomeride exhibits hemihedral facets, whilst crystals of the pure optically active forms do not. Consequently, if formyl-*dl*-*neo*menthylamine deposited a conglomerate of crystals of the pure *d*- and *l*-forms, these crystals would be holohedral and crystallographically identical; since this is not so, the hemihedral crystals which are actually deposited must be regarded as mixed crystals rather than as a conglomerate. When sufficient material becomes available, it will thus be of particular interest to secure a crystallographic examination of pure *d*- and *l*-*iso*hydrobenzoin, which may also prove to be holohedral. Meanwhile, it becomes necessary to revise the opinions which have hitherto prevailed concerning the applicability of Pasteur's method of optical resolution by the mechanical separation of *d*- and *l*-oriented crystals.

FIG. 1.



EXPERIMENTAL.

Optical Resolution of dl-*Diphenylhydroxyethylamine by Condensation with* d-*Oxymethylenecamphor*.—The *dl*-base (m. p. 163°) was prepared from benzoinoxime by the method of Goldschmidt and Polonowska (*Ber.*, 1887, 20, 492). An oily separation of the condensation product occurred almost at once upon mixing equivalent weights of the base and *d*-oxymethylenecamphor, dissolved, respectively, in warm 50% acetic acid and methylated spirit. After the mixture had been kept for 10 minutes on the water-bath, the product was isolated and freed from unchanged material in the usual way (J., 1913, 103, 1516). The resulting viscid syrup crystallised partly when kept in a desiccator; in absolute alcohol ($c = 1{\cdot}2$) it had $[\alpha]_D + 143°$. After three recrystallisations from ether–light petroleum, the solid portion yielded pure d-*diphenylhydroxyethylamino*-d-*methylenecamphor*, consisting of small, colourless prisms, m. p. 146°, $[\alpha]_D + 235°$. The oily fractions furnished by the mother-liquors consisted of somewhat impure *l*-diphenylhydroxyethylamino-*d*-methylenecamphor, and gave values of $[\alpha]_D$ ranging from $+ 99{\cdot}5°$ to $+ 101{\cdot}5°$.

When dissolved in rectified spirit and titrated with bromine (1 mol.), *d*-diphenylhydroxyethylamino-*d*-methylenecamphor readily yielded the hydrobromide of the corresponding *d*-base (J., 1913, **103**, 448). After evaporation to small bulk on the water-bath, the product was shaken with water and benzene: the aqueous layer deposited d-*diphenylhydroxyethylamine hydrobromide* upon evaporation to dryness. This salt crystallises from acetone in long, transparent needles, m. p. 192°, $[\alpha]_D + 59{\cdot}0°$, $[M]_D + 173°$ in aqueous solution ($c = 0{\cdot}5$) (Found: Br, 26·9. $C_{14}H_{15}ON,HBr$ requires Br, 27·2%).

d-*Diphenylhydroxyethylamine*, obtained by precipitating an aqueous solution of the hydrobromide with dilute ammonia, melted at 143° and had $[\alpha]_D + 10{\cdot}0°$, when dissolved in absolute alcohol ($c = 0{\cdot}65$). No mutarotation was noticed in absolute alcohol, but in acetone ($c = 0{\cdot}2$) the original value, $[\alpha]_D + 15{\cdot}1°$, changed to $- 108{\cdot}8°$ in 1·5 hours, and attained the constant value, $- 120{\cdot}8°$, in 6 hours. That the low optical rotation of the free base was not due to partial racemisation was shown by the fact that the *hydrochloride* prepared from it had $[\alpha]_D + 69{\cdot}3°$, $[M]_D + 173°$, in aqueous solution ($c = 0{\cdot}65$).

Benzylidene-d-*diphenylhydroxyethylamine* crystallises from aqueous alcohol in colourless, transparent prisms, m. p. 109°, $[\alpha]_D - 81{\cdot}4°$ in absolute alcohol ($c = 0{\cdot}5$).

When dissolved in rectified spirit and titrated with bromine, crude *l*-diphenylhydroxyethylamino-*d*-methylenecamphor, having $[\alpha]_D + 101{\cdot}5°$, yielded a lævorotatory salt, which after three recrystallisations from acetone gave a specimen of pure l-*diphenylhydroxyethylamine hydrobromide*, m. p. 192°, $[\alpha]_D - 59{\cdot}0°$, $[M]_D - 173°$, in aqueous solution ($c = 0{\cdot}65$).

dl-*Diphenylhydroxyethylamine hydrobromide*, prepared for comparison, crystallised from acetone in small needles, m. p. 184°; it is considerably more soluble than the optically active components.

Benzylidene-dl-*diphenylhydroxyethylamine* separates from ether–light petroleum in long, fine, translucent needles, m. p. 120·5°.

Crystallisation of dl-*Diphenylhydroxyethylamine with Optically Active Acids.*—1. Hot aqueous solutions of the hydrochloride of the *dl*-base (2 mols.) and ammonium *d*-bromocamphorsulphonate (1 mol.) were mixed and allowed to cool. The resulting glistening plates, m. p. 210° (decomp.), appeared to consist of dl-*diphenylhydroxyethylamine* d-*bromocamphorsulphonate* (Found: *M*, by titration, 525. $C_{24}H_{30}O_5NBrS$ requires *M*, 524). The salt was obtained in almost quantitative yield, and the original separations showed values of $[M]_D$ ranging from about + 330° to + 350° in dilute aqueous solution (0·1264 g., made up to 20 c.c., gave α_D + 0·84°, $[\alpha]_D$ + 66·5°, $[M]_D$ + 348°). After one or two recrystallisations from aqueous alcohol, the molecular rotation fell to $[M]_D$ + 273° (0·1018 g., made up to 20 c.c., gave α_D + 0·53°, $[\alpha]_D$ + 52·1°); this value, which is practically coincident with that of the acid ion in dilute aqueous solution (J., 1910, **97**, 2201), was unaffected by further recrystallisation. Specimens of the base liberated from fractions of this salt, and also from the original aqueous filtrate, exhibited no appreciable optical rotation when dissolved in absolute alcohol (0·13 g. in 20 c.c.) and examined in a 2-dcm. tube. The variations in the rotatory power of the *d*-bromocamphorsulphonate thus appear to be attributable to tautomerism on the part of the acid (compare J., 1914, **105**, 800).

2. When evaporated to dryness on the water-bath, an alcoholic solution of equivalent weights of *dl*-diphenylhydroxyethylamine and *d*-camphorsulphonic acid yielded a colourless, crystalline solid. The crude product melted indefinitely at about 190°, and had $[\alpha]_D$ +17·8° in dilute aqueous solution; separations consisting of small prisms were readily deposited from solutions in acetone or chloroform. Five successive recrystallisations from these solvents furnished a pure specimen of d-*diphenylhydroxyethylamine* d-*camphorsulphonate*, m. p. 193°; 0·1213 g., made up to 20 c.c. with water, gave α_D + 0·62°, $[\alpha]_D$ + 51·5°, $[M]_D$ + 227° (Found: *M*, by titration, 447. $C_{24}H_{31}O_5NS$ requires *M*, 445). The calculated molecular rotatory power for the basic ion is thus + 175°, a value which is in excellent agreement with $[M]_D$ + 173°, recorded above for the hydrobromide of the *d*-base. In accordance with this conclusion, specimens of the free base and of the hydrobromide, prepared from the salt *dAd*B, gave optical rotations practically identical with those already recorded.

Owing to its pronounced solubility, the pure diastereoisomeric salt, *dAl*B, could not be isolated. An impure fraction, having $[M]_D$ + 38°, yielded a specimen of crude *l*-diphenylhydroxyethylamine hydrochloride having $[M]_D$ − 13°; this value is practically identical with the calculated value for the basic ion of the fraction in question, and thus it appears that both diastereoisomerides give the normal rotatory powers in dilute aqueous solution.

Action of Nitrous Acid on dl- *and* l-*Diphenylhydroxyethylamine.*—1. A dilute ice-cooled aqueous solution of *dl*-diphenylhydroxyethylamine hydrochloride was treated with the calculated amount of sodium nitrite solution, the reaction being completed on the water-bath. By repeated fractional crystallisation of the partly crystalline product from ether, fractions were isolated which melted at 134° and 118°, and appeared to consist of hydrobenzoin (m. p. 138°) and *iso*hydrobenzoin (m. p. 119°), respectively.

2. *l*-Diphenylhydroxyethylamine hydrobromide upon similar treatment yielded a partly crystalline product, which was extracted with ether and examined polarimetrically in absolute alcohol: 0·2366 g. in 20 c.c. gave $\alpha_D + 0{\cdot}92°$, $[\alpha]_D + 38{\cdot}9°$. The crude product was purified by recrystallisation from light petroleum; the first fraction melted indefinitely between 117° and 130°, and had $[\alpha]_D + 41{\cdot}9°$ in absolute alcohol.

Action of Nitrous Acid on l- *and* d-iso*Diphenylhydroxyethylamine.*—1. *dl-iso*Diphenylhydroxyethylamine (*Annalen*, 1899, **307**, 120) upon resolution with *d*-tartaric acid (*Annalen*, 1904, **337**, 321) gave a separation which after one recrystallisation from boiling water consisted of l-iso*diphenylhydroxyethylamine hydrogen* d-*tartrate*, m. p. 177°, $[\alpha]_D - 42{\cdot}6°$, $[M]_D - 155°$, in water ($c = 0{\cdot}5$). l-iso-*Diphenylhydroxyethylamine*, m. p. 115°, obtained from this salt by precipitation with aqueous ammonia, gave $[\alpha]_D - 125{\cdot}0°$ in absolute alcohol * ($c = 0{\cdot}65$), no mutarotation being observed. In acetone solution ($c = 0{\cdot}6$), a slight mutarotation occurred, the original value, $[\alpha]_D - 102{\cdot}2°$, changing to $- 90{\cdot}3°$ in 3 hours. The *hydrochloride* had $[\alpha]_D - 81{\cdot}7°$, $[M]_D - 204°$, in aqueous solution ($c = 0{\cdot}65$).

When treated with nitrous acid in the cold, as described above, *l-iso*diphenylhydroxyethylamine hydrochloride yielded a partly crystalline product having $[\alpha]_D - 47{\cdot}1°$ in absolute alcohol ($c = 1{\cdot}05$). A wholly crystalline fraction from ether–light petroleum had m. p. 114—125°, $[\alpha]_D - 48{\cdot}0°$; a final purification from hot alcohol yielded a crystalline separation having m. p. 138—142°, $[\alpha]_D - 79{\cdot}7°$.

In a further experiment, carried out at 70° instead of at 0°, a slight excess of sodium nitrite solution was added gradually to *l-iso*diphenylhydroxyethylamine hydrochloride in a dilute aqueous solution containing one equivalent of free hydrochloric acid. Upon cooling, the product consisted of a brown oil, together with a less amount of small, glistening needles having $[\alpha]_D - 80{\cdot}7°$ in absolute alcohol ($c = 0{\cdot}65$), m. p. 137—138°. After recrystallisation from ether–light petroleum, the needles gave $[\alpha]_D$ − 89·1°, m. p. 144°. A final recrystallisation from absolute alcohol yielded small, transparent prisms or leaflets, m. p. 146°, $[\alpha]_D$ − 89·7°; these appeared to consist of l-iso*hydrobenzoin* (Found: C, 78·4; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). A mixture of this substance with the crystals melting at 138—142°, mentioned above, melted at 138—142°.

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* Erlenmeyer (*loc. cit.*), using either *d*-tartaric acid or helicin as the resolving agent, observed $[\alpha]_D \pm 109{\cdot}7°$; by using *d*-camphorsulphonic acid, values of $[\alpha]_D$ as high as $+ 130°$ for the free base have been observed in this laboratory.

2. The crude *d-iso*diphenylhydroxyethylamine obtained by adding ammonia to the mother-liquors from the above resolution with *d*-tartaric acid, when crystallised from aqueous alcohol yielded a final (fourth) small fraction having $[\alpha]_D$ + 125·5° (absolute alcohol); the preceding fractions consisted of the optically impure *d-iso*-base. More of this base was prepared by mixing sodium *l*-tartrate (1 mol.), hydrochloric acid (1 mol.), and *dl-iso*diphenylhydroxyethylamine hydrochloride (2 mols.) in an appropriate quantity of hot water. The ensuing crystalline separation, when recrystallised from hot water, had $[\alpha]_D$ + 43·4° in dilute aqueous solution, and thus consisted of d-iso*diphenylhydroxyethylamine hydrogen* l-*tartrate*, m. p. 177°. The corresponding base had $[\alpha]_D$ + 125·5° (absolute alcohol).

Upon treating *d-iso*diphenylhydroxyethylamine with nitrous acid in the usual way at 0°, the resulting partly crystalline product had $[\alpha]_D$ + 49·7° in absolute alcohol. In preparing pure *d-iso*hydrobenzoin, it was found advantageous, in a further experiment, to add two equivalents of *N*-hydrochloric acid to the reaction mixture before heating on the water-bath to expel the nitrogen. The crystalline deposit formed upon cooling the liquid (0·7 g. from 5·5 g. of base) was readily separated from the accompanying oil: it had $[\alpha]_D$ + 77·0° (absolute alcohol), m. p. 135—139°. Recrystallisation from absolute alcohol yielded small, glistening prisms or leaflets of d-iso*hydrobenzoin*, m. p. 146°, $[\alpha]_D$ + 90·5° in absolute alcohol ($c = 0{\cdot}65$). In view of the sharp melting point and the close agreement of these values with the corresponding data for *l-iso*hydrobenzoin, the preparations may be regarded as optically pure.

Melting-point Curve of Mixtures of d- *and* l-iso*Hydrobenzoin*.—Solid mixtures of known composition were made by mixing and evaporating measured volumes of standard alcoholic solutions of the two components. The equimolecular mixture had a sharp melting point (119°). With the single exception indicated below, the other mixtures melted over a range of at least 5°, and the recorded temperature is that of complete fusion. In all instances, the result was checked by remelting the mixture after it had solidified. The melting points were as follows for mixtures containing the stated percentages of the *d*-enantiomeride: 100, 146°; 90, 139°; 75, 129°; 65, 124°; 55, 119—120°; 50, 119°; 25, 128°. The melting point of pure *dl*-*iso*hydrobenzoin must thus be accepted as 119°; the values quoted in the literature range from 119° to 122°.

We express our indebtedness to the Department of Scientific and Industrial Research for a maintenance grant to one of the authors (C. C. S.). The research is being continued.

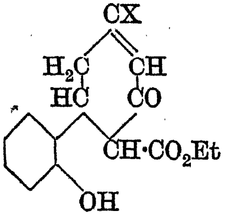
United College of St. Salvator and St. Leonard,
University of St. Andrews. [*Received, March 2nd*, 1927.]

CXXXII.—*The Interaction of Ethyl Acetoacetate with Distyryl Ketones. Part III.* o-*Hydroxychlorodistyryl Ketones.*

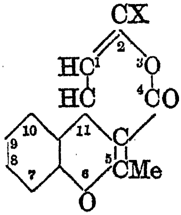
By Isidor Morris Heilbron and Rowland Hill.

Experiments carried out by one of us (J., 1924, **125**, 2064; 1925, **127**, 2159) showed that ethyl acetoacetate reacted with *o*-hydroxydistyryl ketones to give *cyclo*hexenones and that the position taken up by the entering group could be determined by the fact that, when the β-ketonic ester attached itself to the styryl residue adjacent to the *o*-hydroxyl, the carbethoxy-group was eliminated, possibly owing to intermediate coumarin formation. The interactions of ethyl acetoacetate with *2′-chloro-2-hydroxydistyryl ketone* and with the 3′- and *4′-chloro-isomerides* have now been investigated, and the results show that the previous deductions are by no means general. In each case, two products were isolated, a *cyclo*hexenone of molecular formula $C_{23}H_{21}O_4Cl$, and a very small quantity of a second substance of empirical formula $C_{21}H_{15}O_3Cl$, the yield of which decreases progressively as the chlorine atom passes from the ortho- to the para-position. Oxidation of the former by means of potassium permanganate in acetone solution gave the corresponding *o*-, *m*-, or *p*-chlorobenzoic acid, proving that, despite the presence of the carbethoxy-group, addition had taken place at the ethenoid linking adjacent to the *o*-hydroxy-group and consequently the *cyclo*hexenones must be formulated as (I).

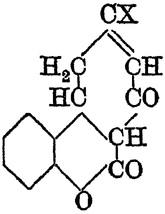
The isomeric substances $C_{21}H_{15}O_3Cl$ may be represented either as *2-chlorostyryl-5-methyl-3 : 4-coumalo-6-benzopyrans* (II), or as chlorostyryldihydrocoumarino*cyclo*hexenones (III), resulting through the elimination of a molecule of alcohol from the corresponding *cyclo*hexenones (I). If the latter formulation be correct, it is reasonable to expect that the conversion of the *cyclo*hexenones into (III) should be possible, but this we have failed to bring about under any of the conditions usually employed for effecting such ring closures. Conversely, attempts to open the supposed dihydrocoumarin ring with formation of the free *cyclo*hexenones have been equally unsuccessful. It would thus seem that these substances cannot be dihydrocoumarino*cyclo*hexenones, and this view is supported by the fact that they fail to give the blood-red coloration with concentrated sulphuric acid characteristic of *cyclo*hexenones of this type (Borsche, *Annalen*, 1910, **375**, 145). They must consequently be formulated in accordance with (II), a type of ring formation reminiscent of that observed by Vorländer (*Annalen*, 1906, **345**, 155) and more recently by Kon and Nutland (J., 1926, 3101), who found that pulegone and *iso*pulegone reacted abnormally with ethyl sodiocyanoacetate, yielding, in place of the expected cyano-esters, the unsaturated cyano-lactones. In order more fully to test this point, 2′-chloro-2-hydroxydistyryl ketone was condensed with benzoylacetic ester. In this case, *cyclo*hexenone formation is precluded, and consequently, if our contentions are correct, a benzopyran and not a dihydrocoumarin derivative should be formed. The product actually isolated proved to be *ethyl* 4-o-*chlorostyracyl-2-phenyl*-1 : 4-*benzopyran-3-carboxylate* (IV), no trace of a dihydrocoumarin being obtained. The non-isolation of the corresponding coumalobenzopyran may possibly have been due to experimental difficulties, since the semi-solid fraction first deposited resisted all attempts at purification.



(I.)



(II.)

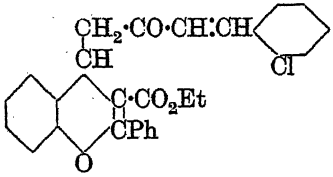


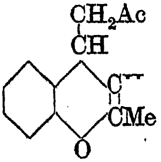
(III.)

(X = *o*-, *m*-, or *p*-$C_6H_4Cl{\cdot}CH{:}CH$.)

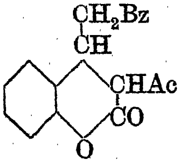
In the case of the *o*-hydroxymonostyryl ketones, the β-ketonic ester must of necessity condense adjacent to the hydroxyl group. Forster and Heilbron have already shown (J., 1924, **125**, 340) that the condensation of 2-hydroxystyryl methyl ketone with ethyl acetoacetate leads to 4-acetonyl-2-methyl-1 : 4-benzopyran (V), and a similar type of reaction occurs between 2-hydroxystyryl phenyl ketone and benzoylacetic ester. With 2-hydroxystyryl phenyl ketone, however, these authors state that the reaction leads, in very poor yield, to 3-acetyl-4-phenacyldihydrocoumarin (VI) together with a solid, m. p. 214°, to which no definite structure was assigned. This reaction has again been investigated under various conditions, but no trace of (VI) has been obtained, *4-phenacyl-2-methyl-*1 : 4-*benzopyran* (VII) being isolated in good yield together with a minute quantity of the substance melting at 214°.

(IV.)

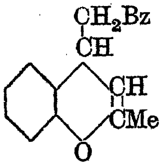




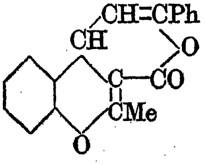
(V.)



(VI.)



(VII.)



(VIII.)

The constitution of the pyran has been definitely settled by the fact that the condensation of acetylacetone and 2-hydroxystyryl phenyl ketone yields the same product, for which the pyran formula alone is possible. Analysis of the substance, m. p. 214°, indicates that its structure corresponds to *2-phenyl-5-methyl-*3 : 4-*coumalo-*6-*benzopyran* (VIII), a result in complete harmony with the preceding observations.

An interesting point emerging from this investigation is the fact that, independent of the position of the chlorine atom, the ethyl acetoacetate enters the molecule of the chlorohydroxy-ketone adjacent to the hydroxyl, thus showing that the polar influence of this group completely overweighs that of the halogen substituent, independent of its position in the other styryl residue. The same holds for the *o*-methoxy-ketone, for from 4′-chloro-2-methoxydistyryl ketone ethyl 3-*o*-methoxyphenyl-5-*p*-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate was formed, identical with the methyl ether prepared by direct methylation of the *cyclo*hexenone obtained from 4′-chloro-2-hydroxydistyryl ketone.

EXPERIMENTAL.

2′-Chloro-2-hydroxydistyryl Ketone.—2-Hydroxystyryl methyl ketone (30 g.) and *o*-chlorobenzaldehyde (30 g.) dissolved in aqueous sodium hydroxide (120 c.c. of 10%), heat being developed and a clear red solution produced. This was cooled, and a further 120 c.c. of alkali slowly added with constant stirring. After 15 hours, the sodium salt of the distyryl ketone, which had separated in red, iridescent crystals, was dissolved in warm water, and the ketone liberated as a flocculent, yellow precipitate by carbon dioxide. *2′-Chloro-2-hydroxydistyryl ketone* crystallised from benzene after treatment with blood charcoal in light yellow needles, m. p. 153° (decomp. to a dark green liquid) (yield, 33 g.). It dissolved in aqueous alkali and in concentrated sulphuric acid to blood-red solutions. In place of the yellow form, the ketone was sometimes obtained as bright green plates (Found: C, 71·6; H, 4·6. $C_{17}H_{13}O_2Cl$ requires C, 71·7; H, 4·6%).

2-o-*Chlorostyryl*-5-*methyl*-3 : 4-*coumalo*-6-*benzopyran* (II).—A mixture of 2′-chloro-2-hydroxydistyryl ketone (20 g.), absolute alcohol (500 c.c.), ethyl acetoacetate (18 c.c.), and aqueous sodium hydroxide (40 c.c. of 20%) was left for 4 days at room temperature, and the orange-red deposit was then collected and repeatedly washed with dilute warm hydrochloric acid and with water. The dried product was crystallised from ethyl acetoacetate and again from much absolute alcohol, from which it separated in long, slender, orange-yellow needles, m. p. 183° (yield, 3·5 g.), sparingly soluble in the usual organic solvents. It dissolved slowly to an orange solution on being warmed with aqueous or alcoholic sodium hydroxide, and in concentrated sulphuric acid it gave an orange-red coloration (Found: C, 71·6, 71·8; H, 4·2, 4·4; Cl, 9·9, 9·9. $C_{21}H_{15}O_3Cl$ requires C, 71·9; H, 4·3; Cl, 10·1%). On boiling under reflux with alcoholic sodium ethoxide, the substance gradually dissolved; acidification then precipitated a solid, which was separated by means of ethyl acetate into two compounds, m. p. 121—122° and 211°, neither of which gave the analytical values required for a *cyclo*hexenone or a pyran derivative. The quantities of these solids were too small to allow of more detailed investigation.

Ethyl 3-o-*hydroxyphenyl*-5-o-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (I) was obtained, as a yellow, gummy mass which slowly hardened, by acidifying the filtrate of the above reaction mixture with dilute hydrochloric acid. After being washed, dried, and repeatedly crystallised from benzene in presence of animal charcoal, it was obtained in minute, yellow needles, m. p. 177—178° (yield, 7·5 g.). It was moderately easily soluble in the usual organic solvents and readily soluble in aqueous alkali and gave an intense red coloration with concentrated sulphuric acid (Found: C, 69·3; H, 5·4. $C_{23}H_{21}O_4Cl$ requires C, 69·6; H, 5·3%). Attempts to convert this *cyclo*hexenone into the corresponding dihydrocoumarino*cyclo*hexenone (III) by treatment with aqueous or alcoholic sodium hydroxide, by the use of sodium in xylene and by other means were unsuccessful.

Oxidation.—The hydroxy-*cyclo*hexenone (I) (1 g.), dissolved in acetone (75 c.c.), was treated with potassium permanganate in small quantities; *o*-chlorobenzoic acid, m. p. 134—135°, was isolated from the reaction mixture.

3-o-*Hydroxyphenyl*-5-o-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one.*—The ester (I) (1 g.) was dissolved in glacial acetic acid (20 c.c.) and boiled for 2 hours with sulphuric acid (10 c.c. of 20%). The resultant deep red liquid was poured on a mixture of ice and water, and the precipitated *cyclo*hexenone repeatedly crystallised from ethyl acetate, from which it separated in clusters of yellow plates, m. p. 209—210° (Found: C, 73·8; H, 5·4. $C_{20}H_{17}O_2Cl$ requires C, 74·0; H, 5·2%).

3'-*Chloro-2-hydroxydistyryl Ketone.*—The preparation was similar to that of the isomeric 2'-chloro-compound. The sodium salt separated completely, after 15 hours, in black plates with a brilliant green reflex. The *ketone* crystallised from benzene in golden-yellow plates (yield, 72%), m. p. 142—143° (decomp. to a dark green liquid) (Found: C, 71·6; H, 4·6%). This compound also exists in a green modification.

2-m-*Chlorostyryl-5-methyl-3*: 4-*coumalo-6-benzopyran,* after preliminary purification from ethyl acetoacetate, crystallised from absolute alcohol in aggregates of orange-red needles, m. p. 170°, which are sparingly soluble in the ordinary organic solvents (yield, 8%) (Found: C, 71·5; H, 4·4%).

Ethyl 3-o-*hydroxyphenyl*-5-m-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* was obtained from the filtrate and separated from benzene in small, yellow cubes (yield, 30%), m. p. 169° (Found: C, 69·5; H, 5·5%). Oxidation with potassium permanganate in cold acetone solution yielded *m*-chlorobenzoic acid, m. p. 148—149°. 3-o-*Hydroxyphenyl*-5-m-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one* crystallised from ethyl acetate in bright yellow rhombs, m. p. 221° (Found: C, 73·7; H, 5·5%).

4'-*Chloro-2-hydroxydistyryl ketone* crystallised from benzene, after treatment with charcoal, in pale yellow plates (yield, 67%), m. p. 152° (decomp. to a dark green liquid) (Found: C, 71·8; H, 4·8%).

2-p-*Chlorostyryl-5-methyl-3*: 4-*coumalo-6-benzopyran* crystallised with difficulty from ethyl acetoacetate in clusters of cream-coloured needles (yield, 1%), m. p. 261—262° (Found: C, 72·1; H, 4·1%). It dissolves in concentrated sulphuric acid to an orange-red solution and is very sparingly soluble in the usual organic solvents.

From the filtrate from which the above compound was separated, *ethyl* 3-o-*hydroxyphenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* was obtained as a brown gum on rendering the solution acid. It was repeatedly crystallised from benzene and from ethyl acetate–light petroleum and was thus obtained in large, golden-yellow plates (yield, 33%), m. p. 199—200° (Found: C, 69·7; H, 5·5%). On oxidation with potassium permanganate in acetone solution it gave *p*-chlorobenzoic acid, m. p. 237°. Methylation with methyl sulphate in acetone solution yielded the methyl ether (m. p. 160°) identical with that obtained by the direct condensation of 4′-chloro-2-methoxydistyryl ketone with ethyl acetoacetate.

3-o-*Hydroxyphenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one* was readily obtained by hydrolysing the above ester with 20% sulphuric acid in acetic acid solution. It separated from ethyl acetate in yellow prisms, m. p. 176° (Found: C, 74·3; H, 5·2%).

4′-*Chloro*-2-*methoxydistyryl Ketone.*—The dry sodium salt of 4′-chloro-2-hydroxydistyryl ketone, prepared by condensation as already described, was dissolved in acetone and heated with a slight excess of methyl iodide under reflux for 1 hour. After removal of sodium iodide, the reaction mixture was diluted with water; the yellow oil that separated solidified on being scratched and then crystallised from aqueous acetone in slender, yellow needles, m. p. 74—75° (yield from sodium salt, 92%) (Found: C, 72·5; H, 5·2. $C_{18}H_{15}O_2Cl$ requires C, 72·4; H, 5·0%).

Ethyl 3-o-*Methoxyphenyl*-5-p-*chlorostyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate.*—The above ketone (5 g.) was dissolved in absolute alcohol (40 c.c.) and refluxed for 3 hours on a water-bath with ethyl acetoacetate (3 g.) and alcoholic sodium ethoxide (1·6 g.). The hot solution, which was filtered from a small quantity of sodium carbonate, deposited, on cooling, an orange-yellow solid; this was crystallised from methyl alcohol, the cyclo*hexenone* (4 g.) being obtained in small, yellow, rhombohedral plates, m. p. 160° (Found: C, 69·8; H, 5·7. $C_{24}H_{23}O_4Cl$ requires C, 70·2; H, 5·6%). The solution in concentrated sulphuric acid is carmine-red.

Ethyl 4-o-*Chlorostyraeyl*-2-*phenyl*-1 : 4-*benzopyran*-3-*carboxylate* (IV).—A hot solution containing 2′-chloro-2-hydroxydistyryl ketone (10 g.), ethyl benzoylacetate (9 g.), and alcohol (50 c.c.) was treated with sodium ethoxide solution (1·7 g. of Na), and the whole left at room temperature for 60 hours. The reaction mixture was then diluted with water and separated from a small quantity of a dark-coloured oil, which gradually solidified but resisted subsequent efforts at purification. The filtrate was diluted to 2000 c.c. and mechanically stirred for several days. On addition of sodium chloride (100 g.), a yellow solid was precipitated which, when crystallised repeatedly from absolute alcohol, separated in colourless needles, m. p. 144—145°. These contain half a mol. of alcohol of crystallisation, which is removed on heating for 5 hours at 110°; the anhydrous compound melts at 195°. The substance slowly dissolves on warming with aqueous sodium hydroxide and gives a yellow solution with concentrated sulphuric acid (Found : C, 73·0; H, 5·2. $C_{28}H_{23}O_4Cl$ requires C, 73·3; H, 5·0%).

2-Phenyl-5-methyl-3 : 4-coumalo-6-benzopyran (VIII).—A mixture of 2-hydroxystyryl phenyl ketone (11 g.), ethyl acetoacetate (6·5 c.c.), and alcohol (100 c.c.) was treated with alcoholic sodium ethoxide (2·5 g. of Na), and the red solution kept for 18 hours at room temperature. The small quantity of brown solid which separated on dilution with water was repeatedly crystallised from benzene in presence of blood charcoal. The pure substance was thus obtained, in very small yield, in colourless needles, m. p. 214° (Found : C, 78·9; H, 4·6. Calc. for $C_{19}H_{14}O_3$: C, 78·6; H, 4·8%). These figures agree well with those given by Forster and Heilbron (*loc. cit.*, p. 345).

*4-Phenacyl-2-methyl-*1 : *4-benzopyran* (VII) was precipitated from the filtrate of the above reaction mixture on addition of dilute hydrochloric acid. The brown, gummy mass was allowed to harden and repeatedly crystallised from absolute alcohol in the presence of blood charcoal. The *pyran* forms colourless plates, m. p. 171°, which are moderately easily soluble in alcohol, insoluble in cold aqueous alkali, but readily soluble in the hot solution (Found : C, 81·5; H, 6·0. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Condensation of Acetylacetone with 2-Hydroxystyryl Phenyl Ketone.—A boiling solution of 2-hydroxystyryl phenyl ketone (7·5 g.) in alcohol (30 c.c.) and aqueous sodium hydroxide (7·5 c.c. of 40%) was treated with acetylacetone (6 g.) and refluxed for 30 minutes; a further quantity of acetylacetone (6 g.) was then added. After 1 hour, a small quantity of inorganic matter was removed, and the clear solution, on cooling, deposited a mass of yellow needles; a further quantity was obtained by diluting the filtrate. The combined fractions crystallised from alcohol in large, colourless plates, m. p. 169—170°. A mixed melting point with 4-phenacyl-2-methyl-1 : 4-benzopyran, prepared as described above, showed no depression.

We desire to express our thanks to the United Alkali Co., Ltd., for a grant to one of us (R. H.) which enabled this research to be carried out.

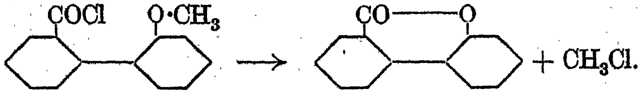
THE UNIVERSITY, LIVERPOOL. [*Received, March 9th,* 1927.]

CXXXIII.—1-*Methoxydiphenyl*-1'-*carboxylic Acid and its Demethylation with Thionyl Chloride.*

By HAROLD GORDON RULE and EGON BRETSCHER.

1-METHOXYDIPHENYL-1'-CARBOXYLIC acid is readily obtained by methylating the lactone of 1-hydroxydiphenyl-1'-carboxylic acid, but the latter substance is unfortunately only available in poor yield (Richter, *J. pr. Chem.*, 1883, **28**, 284; Graebe, *Annalen*, 1895, **284**, 316; Borsche, *Annalen*, 1900, **312**, 225). The reaction between *o*-iodophenyl *o*-iodobenzoate and copper powder at 250° gave very little of the lactone, and under the same conditions, the corresponding bromo-compound failed to react at all. A modification of Borsche's method in which the diazonium sulphate of phenyl *o*-aminobenzoate was warmed in aqueous solution with copper powder produced the lactone in only 14% yield and therefore offers no advantage over that of Borsche (*loc. cit.*).

An unexpected reaction was encountered in an attempt to esterify 1-methoxydiphenyl-1'-carboxylic acid by way of the acid chloride —warming for a few minutes with thionyl chloride demethylated the methoxy-acid quantitatively to the lactone of the hydroxy-acid:



A similar, although less complete, change occurred when the acid was kept for 2 or 3 days with excess of thionyl chloride at room temperature, and when the dried sodium salt was allowed to react at a low temperature with thionyl chloride.

The ease with which this reaction proceeds is remarkable and is presumably due to the close proximity of the –COCl and –OMe groups. Numerous examples of demethylation are recorded in the literature, but these commonly require for their completion several hours' heating at temperatures ranging from 120° to 200°.

EXPERIMENTAL.

Preparation of the Lactone of 1-*Hydroxydiphenyl*-1'-*carboxylic Acid from Phenol and Anthranilic Acid.*—The lactone was prepared according to the directions of Borsche (*loc. cit.*), but the purification was more effective when the dark red product was dissolved in ether and washed several times with ammonia, which also completely removed the colouring matter. After being dried with calcium chloride, the ethereal solution gave the lactone, which, after recrystallisation from light petroleum, melted at 94—95°. The yield from 60 g. of anthranilic acid and 220 g. of phenol varied from 8·0 to 11·3 g.

Preparation of the Lactone from Phenyl o-*Aminobenzoate*.—Phenyl *o*-aminobenzoate was prepared in 76% yield by reducing phenyl *o*-nitrobenzoate in alcoholic solution with tin and hydrochloric acid. The reduction is complete in 5 minutes; longer treatment results in loss, owing to hydrolysis of the ester.

The diazotisation also is best conducted in alcoholic solution with amyl nitrite. A solution of phenyl *o*-aminobenzoate (10 g.) in absolute alcohol (120 c.c.) containing the necessary amount of concentrated sulphuric acid (5·0 g.) was cooled to 5°, when crystals of the sulphate separated, and amyl nitrite (5·4 g.) was added. After 2 hours the diazonium sulphate was precipitated with ether (240 c.c.), filtered off, and dried (yield, 13·6 g.).

To a solution of the diazonium salt in 100 c.c. of water, 50 g. of copper powder were slowly added, evolution of nitrogen occurring; the temperature was then raised to 40° during 4 hours. When no more diazonium compound could be detected, the mixture of solids was filtered off, dried, and extracted with chloroform. The solvent was then removed from the extract, the residue hydrolysed with alcoholic potash, and the alkaline liquid acidified. From the mixture of lactone, phenol, and salicylic acid thus obtained, phenol was removed by rapid distillation in steam, which also carried over a little of the lactone, and the liquid was made alkaline with sodium carbonate and extracted with ether. The solution was dried, and on removal of the solvent gave the pure lactone, m. p. 93—94°.

The yield varied with the nature of the copper powder. Ten g. of amino-ester, after diazotisation, gave no lactone at all on treatment with Kahlbaum's "Naturkupfer C." Copper powder which had been prepared according to Gattermann (*Ber.*, 1890, **23**, 1218) and had been dried before use gave 0·8 g. of lactone, whereas the freshly prepared moist powder gave a yield of 1·3 g. (14% of the theoretical).

1-*Methoxydiphenyl*-1'-*carboxylic Acid*.—The solution obtained by heating 10 g. of the lactone with 20 g. of 30% aqueous sodium hydroxide was cooled and shaken for 1 hour with 19 c.c. of methyl sulphate. The methyl ester of the methoxy-acid that separated as an oil was extracted with ether. The aqueous solution deposited on acidification a mixture of the methoxy-acid with a little lactone, from which the pure acid was extracted with sodium carbonate. The *methoxy-acid* crystallised from benzene as a white, crystalline powder, which is very sparingly soluble in water; m. p. 152—153°

(corr.) (yield, 3·5 g.) (Found: C, 73·7; H, 5·5. $C_{14}H_{12}O_3$ requires C, 73·65; H, 5·3%).

The *methyl* 1-*methoxydiphenyl*-1′-*carboxylate* obtained from the above methylation formed a colourless, viscous liquid, b. p. 181—182°/13 mm. (yield, 6·0 g.). It was readily hydrolysed to the methoxy-acid (Found: C, 74·3; H, 6·0. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%).

Reaction with Thionyl Chloride.—The thionyl chloride employed was the purified product supplied by the British Drug Houses, Ltd. For confirmatory experiments it was again purified by successive distillations over quinoline and beeswax.

(1) The methoxy-acid (3·10 g.) was heated for a few minutes with an equal weight of thionyl chloride. A considerable quantity of hydrogen chloride was evolved and the excess of thionyl chloride was then removed by warming in a vacuum. The residual crystalline mass, alone or mixed with the pure lactone, melted at 92—93° (yield, 2·63 g. Theoretical yield, 2·69 g.).

(2) The dried, finely powdered sodium salt (12 g.) of the methoxy-acid was added in small portions to 15 g. of thionyl chloride, cooled in ice. On allowing the temperature to rise to that of the room, a slow reaction took place, accompanied by a small evolution of gas. After 3 hours, the thionyl chloride was removed in a vacuum, the residue extracted with benzene at 35°, and the extract treated with menthol and pyridine at 100° for several hours. No menthyl ester could be isolated from the reaction mixture, but 6 g. of crude lactone were recovered, m. p. 85—87°. (A further small quantity was carried over during the steam distillation of the menthol.) A mixture of this with the pure lactone melted at 91—92°.

(3) The methoxy-acid (3·90 g.) was kept for 2—3 days at room temperature with thionyl chloride (10 c.c.), and the unchanged thionyl chloride was then removed in a vacuum, without heating. The residue was a crystalline mass of m. p. 78·5—91·5°, a portion of which, after being warmed for a few minutes in air at 40—45°, melted at 87—91·5° (yield, 3·43 g. Lactone formation requires 3·35 g.). A few decigrams of crude methoxy-acid, together with crude lactone, were recovered by treating part of the product, which still smelt of acid chloride, with water and shaking the mixture with sodium carbonate. Altogether about 2 g. of the pure lactone were recovered. A very small quantity of an unidentified acidic compound containing sulphur was also isolated.

The methoxy-acid was not changed by boiling it for several hours with a saturated aqueous-alcoholic solution of hydrochloric acid, and esterification could be effected in the usual way with dry hydrogen chloride as catalyst.

The authors desire to thank the Earl of Moray Fund for a grant which has covered most of the expense incurred during this investigation.

UNIVERSITY OF EDINBURGH. [*Received, February 17th,* 1927.]

NOTES.

The Mechanism of the Reaction between Aluminium, Iodine, Ethyl Alcohol, and Water. The Preparation of Ethyl Iodide. By A. O. JONES and G. MELLING GREEN.

FURTHER work has thrown much light on the chemistry of the above reaction (J., 1926, 2760). What was thought to be a series of reactions involving the formation of an organo-aluminium complex has shown itself to be one proceeding according to the following scheme:

$$\text{Aluminium} + \text{Iodine} \longrightarrow \text{Aluminium iodide.}$$

$$\text{Aluminium iodide} \overset{\text{Hydrolysis}}{\rightleftharpoons} \text{Hydrogen iodide} + \mathrm{Al(OH)_3}.$$

$$\text{Hydrogen iodide} + \begin{cases} \text{Aluminium} \\ \\ \text{Ethyl alcohol} \end{cases} \longrightarrow \begin{cases} \text{Aluminium iodide} \\ \text{Ethyl iodide} \\ \text{Hydrogen.} \end{cases}$$

Thus the main products of the reaction are ethyl iodide, aluminium iodide, and hydrogen, the hydrogen iodide produced by the hydrolysis of the aluminium iodide distributing itself between the ethyl alcohol and the aluminium in a ratio which depends upon the concentration of the water in the alcohol used.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, January 7th,* 1927.]

New Fluorides of Selenium. By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX.

Selenium oxyfluoride has been prepared by the action of dry silver fluoride on selenium oxychloride in a platinum bottle, with subsequent distillation and condensation in a platinum condenser (water-cooled). It is a colourless, fuming liquid, with an ozone-like odour similar to that of some organic compounds which have been treated with fluorine. It was analysed after decomposition with water, both by titration with two indicators (J., 1926, 170) and by gravimetric methods. Three separate analyses on quantities of about 1 g. gave the following results, the weights of selenium and fluorine found being referred to the weights of compound taken in calculating the percentages: Se, 59·1, 59·3, 59·9 (as Ag_2SeO_3); F, 28·3, 28·2, 28·3 (volumetric), 28·3 (as CaF_2). Hence Se (mean), 59·4; F (mean), 28·3 ($SeOF_2$ requires Se, 59·5; F, 28·5%).

Selenium tetrafluoride has been prepared by the same method from silver fluoride and selenium tetrachloride. The first reaction is violent and distillation of the product gives a colourless, fuming liquid having much the same appearance and smell as the oxyfluoride. The first portion of the distillate, collected separately, was deep red, and possibly may contain a lower fluoride, Se_2F_2, formed by the reducing action of the silver present in the silver fluoride. 0·998 G. of this liquid was analysed as described above: Se, 51·8 (as Ag_2SeO_3), 50·6 (as Se); F, 45·5 (volumetric), 46·7 (volumetric HF with gravimetric Se), 46·9 (as CaF_2). Hence Se (mean), 51·2; F (mean), 46·3 (SeF_4 requires Se, 51·0; F, 49·0%).

The properties and reactions of these compounds are being further examined.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, February* 26*th*, 1927.]

Studies of Precipitated Solids, especially of Strontium and Calcium Sulphates. By PETR P. VON WEIMARN.

THE statement by Bertram Lambert and his collaborators W. Hume-Rothery and J. Schaffer (J., 1926, 2637, 2648) that, previous to their work, no "detailed or systematic study of the effects of the conditions of precipitation upon the type, nature and size of the precipitated particles of strontium sulphate and of calcium sulphate had been carried out" is incorrect. As far back as 1905 I had begun a systematic study of the effects of the conditions of precipitation upon the type, nature, and size of the precipitated particles of different salts. My paper published in 1906 (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 264) included strontium and calcium sulphates amongst the 62 salts investigated, and announced the law that *the mean size of the precipitated crystals decreases with increasing concentration of the reacting solutions*, provided, and this is very important, that the crystallisation process is complete and the course of the process is not disturbed by the influence of variables foreign to the normal reaction. The graphic representation of this law is a curve without a maximum. Curves with maxima are obtained only if the crystallisation process is not complete, if aggregates of crystals are mistaken for individual crystals, or if variables foreign to the normal precipitation process exert an influence.

From the beginning of 1906 my results were published periodically (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 624; *Annals Mining Inst. S. Petersburg*, 1908, **1**, 239; *Jap. J. Chem.*, 1926, **3**, 20; *Koll.-Chem.*

Beih., 1923, **18**, 44, and succeeding years; *Chem. Reviews*, 1925, **2**, 217). Particular mention, with photomicrographs, of the precipitation of strontium and calcium sulphates occurs in my book "Kolloides und Kristalloides Lösen und Niederschlagen," Vol. II, pp. 661—680 and Figs. 90, 91 (Kioto, 1921), and in the second edition of Volume I of this book, "Die Allgemeinheit der Kolloidzustandes," Figs. 92, 93 (Dresden, 1925).

The investigations of Lambert and his collaborators of precipitates of calcium and strontium sulphates are important as independent confirmation of previous work, and are in some respects more detailed. I believe, however, that in other points my investigations (*Koll.-Chem. Beih.*, 1923, **17**, 27) were more extensive, as they included wider limits of concentration and alcoholic as well as aqueous solutions, and colloidal solutions of both salts were obtained.

Subsequently, between 1919 and 1926, detailed investigations of precipitated solids were carried out by Sven Odén (Svedberg, "Formation of Colloids," London, 1921, pp. 94—100, Fig. 20; *Z. Koll.*, 1926, **40**, 92), confirming my results, the latter paper including the examination of strontium sulphate.

As far as I know the literature on the subject, Lambert and his collaborators were the first to study by crystallographic measurement the influence of anions and kations on the precipitation of calcium and strontium sulphates from aqueous solutions and also the influence of certain factors on the transformation of hydrates of strontium sulphate into the anhydrous salt, although I had studied in detail the influence of ions on barium sulphate precipitated from 48% alcohol.—THE IMPERIAL INDUSTRIAL RESEARCH INSTITUTE, OSAKA, JAPAN. [*Received, March 2nd*, 1927.]

Separation of d-*Neobornylamine from* d-*Bornylamine*. By JOHN AUGUSTUS GOODSON.

IT has been shown by Forster (J., 1898, **73**, 390) that reduction of *d*-camphoroxime with sodium in boiling amyl alcohol yields a mixture of *cis*- and *trans*-isomerides, distinguished as *d*-bornylamine and *d*-neobornylamine, respectively. The isolation of *d*-neobornylamine from this mixture has presented considerable difficulty (compare Forster and Hart-Smith, J., 1900, **77**, 1152; Pope and Read, J., 1910, **97**, 987; 1913, **103**, 454). Separation of the two amines can be effected in the following way.

A mixture of the two amine hydrochlorides (223 g.), resulting from the reduction of *d*-camphoroxime (290 g.), on recrystallisation from water gave a crop of crystals (77·3 g.). An ethereal solution of the bases from the crystals was shaken consecutively with 500 and 300 c.c. of dilute hydrochloric acid (approx. 0·6*N*), giving solutions 1 and 2. A similar solution of the bases from the mother-liquor was shaken with three quantities of 500 c.c. of the dilute acid, giving solutions 3, 4, and 5. These five preparations were evaporated to dryness, giving the following products:

No.	Weight.	$[\alpha]_D$ in dry alcohol (c = 4·4).	Bornylamine hydrochloride. Calc.	Neobornylamine hydrochloride. Calc.
1	49·8 g.	+19·1°	46·9 g.	2·9 g.
2	27·5	+12·9	23·6	3·9
3	50·85	+ 3·7	37·15	13·7
4	50·35	− 6·2	29·9	20·45
5	44·5	−22·6	16·6	27·9

Pure *d*-bornylamine hydrochloride was easily obtained from the dextrorotatory fractions by recrystallisation from water as shown by Forster (*loc. cit.*) and Frankland and Barrow (J., 1909, 95, 2017). The specimen giving the highest rotation had $[\alpha]_D^{20^\circ}$ + 23·3° (c = 4·4 in dry alcohol), the previous highest value recorded being + 22·7° (Forster, *loc. cit.*). The ethereal solutions of the bases from the lævorotatory fractions were shaken with small quantities of dilute hydrochloric acid until the $[\alpha]_D$ of the hydrochloride of the base remaining in the ethereal solution became constant. *d*-Neobornylamine hydrochloride having $[\alpha]_D^{20^\circ}$ − 49·4° (c = 4·4 in dry alcohol) was thus obtained, the previous highest value recorded being − 44·2° (Forster and Hart-Smith, *loc. cit.*).—WELLCOME CHEMICAL RESEARCH LABORATORIES. [*Received, March 19th*, 1927.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 24TH, 1927, AT 4 P.M.

PROFESSOR H. BRERETON BAKER, C.B.E., D.SC., F.R.S., President, in the Chair.

The Report of the Council for 1926—1927, together with the Balance Sheets and Statements of Accounts for 1926, was presented, and a statement on the finances of the Society made by the Treasurer. The adoption of the Report was proposed by Mr. E. GRANT HOOPER, seconded by Mr. J. H. COSTE, and carried unanimously.

REPORT OF COUNCIL, 1926–1927.

I. *Fellowship Statistics.*

ON the 31st December, 1925, the number of Fellows was 4083. During the year 1926, 242 Fellows were elected and 16 reinstated, giving a gross total of 4341. The deaths recorded in 1926 were 32, as compared with 40 in 1925, and the resignations 101, as against 88; while the names of 115 Fellows have been removed for non-payment of Annual Subscriptions, the corresponding figure last year being 105. The number of Fellows, therefore, at the 31st December, 1926, was 4093, showing an increase of 10 over the previous year. There are also 23 Honorary Fellows.

During the year the Society has lost one of its distinguished Past-Presidents, Sir William Tilden, who held the office of President from 1903 to 1905, was Treasurer from 1899 to 1903, and served on the Council for a total of 37 years; while by the death of Mr. Josiah W. Kynaston (elected in 1859) the Society has lost its oldest Fellow. The Council has to mourn also the loss of a distinguished Foreign Fellow, Professor Kamerlingh Onnes, who was elected in 1920. A lecture in honour of the memory of Kamerlingh Onnes was delivered by Professor Ernst Cohen, Honorary Fellow, on 10th February, 1927, while an obituary notice of Sir William Tilden will appear in due course in the Journal. The Council would again take the opportunity of recording its appreciation of the services rendered by those Fellows who are good enough to undertake the preparation of the obituary notices for the Journal.

The congratulations of the Society have been conveyed to the following who have attained their jubilee as Fellows:

	Elected.
Henry Chapman Jones	May 4th, 1876.
Harold Holcroft	June 1st, 1876.
Charles Alexander Buckmaster	June 1st, 1876.
Walter Hibbert	June 1st, 1876.

	Elected.
Charles George Matthews	June 15th, 1876.
Channell Law	Nov. 16th, 1876.
Walter Charles Davis	Dec. 7th, 1876.
Arthur Pearson Luff	Feb. 15th, 1877.
Frank Watson Young	Mar. 15th, 1877.

II. *Publications.*

The Journal for 1926 contained 3248 pages, of which 3089 pages were occupied by 437 memoirs and 29 notes, the remaining 159 pages being devoted to Obituary Notices, three lectures, the Report of the General Meeting, and the Presidential Address. The Volume for 1925 contained 409 memoirs and 32 notes, and occupied 2902 pages. During 1926, 528 papers were offered to the Society for publication in the Journal, of which 35 were declined, the corresponding numbers for 1925 being 507 and 37, respectively. The average length of the memoirs for 1926 was 7·0 pages, this being the same as for 1925.

The last Report of Council contained mention of the unsatisfactory arrangements in force for editing the Journal, stating that the matter was receiving attention. After due consideration the Council came to the conclusion that the only way in which adequate editorial assistance could be afforded was to appoint, as a part-time officer, an Assistant Editor, whose duty it should be to relieve the Editor of some of the work and edit the Journal during the absence of the Editor on holiday or through illness. The post was offered to Dr. A. D. Mitchell, who took up his duties in March.

The Council has again to record its indebtedness to those Fellows who undertake the refereeing of papers. Some idea of the magnitude of the work carried out so willingly and efficiently will be obtained if it be borne in mind that each of the 528 papers received during 1926 was submitted to two referees.

III. *Library.*

Excluding the evenings on which meetings of the Chemical Society were held, there were 7692 attendances during the past year, as compared with 6994 in 1925; of these, 5273 were made by Fellows of the Chemical Society and 2419 by members of Contributing Societies, as against 2248 the previous year; while the number of books borrowed during 1926 was 5353, as against 4950 in 1925.

Additions to the Library comprise: 295 books, of which 111 were presented, 593 volumes of periodicals, and 48 pamphlets; the corresponding figures in 1925 being 265, 609, and 163, respectively.

The Library now contains 30,899 volumes, consisting of 9361 books and 21,538 bound volumes of periodicals.

The facilities for "Photostat" copying continue to be increasingly utilised, 2084 pages of printed matter having been copied, as against 1266 pages in 1925.

IV. *General.*

In the last Report of Council, the hope was expressed that the decision to hold the Annual General Meeting and Dinner from time to time elsewhere than in London would commend itself to Fellows resident in the provinces. It is satisfactory to report that the attendance at the Annual General Meeting held in the University of Manchester and at the Dinner at the Midland Hotel was such as to justify the Council in the course taken. The appreciative thanks of the Council have been conveyed to the local Committee, which undertook the arrangements for the meeting and the dinner.

In addition to the Kamerlingh Onnes Memorial Lecture, two lectures have been delivered during the year. An informal lecture was given in the Society's Rooms on April 29th, 1926, by Professor W. E. S. Turner on "The Physical Properties of Glasses; the Relationship of Chemical Composition and Mode of Preparation," and the Hugo Müller Lecture was delivered at the Institution of Mechanical Engineers by Professor S. P. L. Sörensen, of Copenhagen, who took as the title of his lecture "The Composition and Characterisation of Genuine Proteins."

The lectures continue to be well attended by Fellows, and the Council is deeply indebted to those who place their services at the disposal of the Society in this connexion.

Professor Richard Willstätter, of Berlin, has accepted the invitation of the Council to deliver the Faraday Lecture for 1927, entitled "Problems and Methods in Enzyme Research," to be given at the Royal Institution (by kind permission of the Managers) on the 18th May.

The Society was represented by Professor H. E. Armstrong and Sir William Pope at the Congress of Pure and Applied Chemistry and the Cannizzaro Celebrations, organised by the Associazione Italiana di Chimica, held in Palermo in May; an Address of Congratulation was presented. The President attended as the Society's delegate the Congress of Chemists held in London in July; while at the 6ème Congrès de Chimie Industrielle, held in Brussels in September, the Society was represented by Professor C. S. Gibson and Professor J. F. Thorpe. An Address of Congratulation was presented to the University of Sheffield on the occasion of its Coming-of-Age Celebrations, which the President and the Treasurer attended on behalf of the Society, and also to the American Chemical

Society at the Celebrations of its 50th Anniversary held in Philadelphia in September.

Professor C. S. Gibson, Sir William Pope, and Professor J. F. Thorpe were appointed the Society's delegates on the Federal Council for 1927; Dr. T. Slater Price agreed to represent the Society for two years on the Editorial Board of the "Journal of Physical Chemistry," in the place of Professor T. M. Lowry, the Faraday Society being represented by Dr. E. K. Rideal; while Professor C. S. Gibson was nominated to give evidence on behalf of the Society before the Sub-Committee appointed to consider the existing practice relating to the method of preparing the British Pharmacopœia.

The Society's representatives on the Bureau of Chemical Abstracts for the year 1926—1927 are Professor C. S. Gibson, Dr. J. T. Hewitt, Professor G. T. Morgan, and Professor J. F. Thorpe.

The year 1926 has seen the introduction of the larger format for the "A" section of "British Chemical Abstracts," a change which, although perhaps unwelcome at first to some Fellows, represents a definite advance towards the co-ordination of chemical publication in this country. The first Annual Index covering abstracts in both pure and applied chemistry, rendered possible by the unification of format, has been prepared and will be issued in due course. The elimination of the overlap as between the "A" and "B" sections, and other changes of a minor character, such as the reduction of the space between successive abstracts and the condensation of the monthly author index, constitute definite economies in the cost of producing the "A" abstracts.

The hearty thanks of the Council have been conveyed to Mrs. Alec Tweedie, who has presented to the Society a valuable portrait in oils of Liebig by Trautschold, together with some of his original letters. Particular interest is given to the portrait, which hangs on the walls of the staircase, by the fact that it is the only oil painting for which Liebig sat. Valuable additions have been made to the Society's collection of medals by the presentation of those awarded to the late Sir Edward Thorpe, and of the Le Blanc, Mond, and other medals.

The Longstaff Medal for 1927 has been awarded to Professor Robert Robinson for his researches in Organic Chemistry. The Harrison Memorial Prize Selection Committee has made its first award, nominating Dr. Charles R. Harington as the recipient of the Harrison Memorial Prize for 1926 for his work on thyroxine. Presentation of these two awards will be made at the Annual General Meeting.

After consideration of the question of limiting the term of service by Fellows on the various Committees, the Council decided that as from April next no Fellow other than an Officer shall serve for more than five consecutive years on any Committee.

The Council desires to thank those Fellows and others who have agreed to contribute to the Annual Reports for 1926.

The Council Room has been relighted and re-decorated, and two walls have been lined with adjustable steel bookshelves. The portraits of Past-Presidents which, it was stated in the last report, would be placed in a portfolio, have been re-hung in the Meeting Room, thus rendering it unnecessary, in the opinion of the Council, for the names of the Past-Presidents to be inscribed on oak panels.

The Council received in April a request from Col.-Sergt. G. V. Holland to be allowed to retire in September, by which time he would have completed 24 years' service. The resignation was accepted with much regret, and in recognition of his loyal services the Council has granted a pension of £120 while Col.-Sergt. and Mrs. Holland are both alive; in event of the death of either, the proportion of the pension to be paid to the survivor will be determined by the Council then in office. A suitably inscribed tea-tray and a purse of £66 0*s.* 6*d.*, to which members of Council and other Fellows had been invited to subscribe, were also presented to him.

The applications for Research Grants received during the year amounted to £1337 15*s.*, the sum granted being £772 (see Proceedings 1926, pp. 84 and 128). It has been decided that in future every applicant who is carrying out the research under direction should have the application initialled by his supervisor, and that if a grant be made to anyone whose permanent residence is not in this country, the supervisor, under whom the Grantee is working, shall be asked to receive the Grant and to assume responsibility for the furnishing by the Grantee of a proper report.

Financial.

The balance representing excess of ordinary income over ordinary expenditure is £135, but there is a nominal adverse balance representing excess of extraordinary expenditure over extraordinary income of £421. This is due to the cost of providing new book-cases in the Council Room (£221), which has been carried to Balance Sheet, and to the transfer of £200, part of last year's balance, from the General Purposes Balance Sheet to the Staff Pensions Fund Balance Sheet.

Income. The ordinary income of the Society has increased during the year by £612 4*s.* 3*d.* This new income has chiefly been derived from the following sources: (1) Increase in annual subscriptions, £234; (2) increase from sales of publications, £370 2*s*. 1*d*. and (3) an advance of £139 2*s*. 4*d*. in the income derived from the Publications Fund. There have, however, been decreases in the incomes obtained by the sale of the Journal to the public and from advertisements.

Expenditure. The ordinary expenditure of the Society has increased by £943 8*s*. 6*d*. over that of 1925. The chief cause of this increase is to be found in the cost of the Journal, which is £405 16*s*. 8*d*. greater than last year. The appointment of a part-time Assistant Editor in March accounts for £153 17*s*. of this increase, the remainder, £251 19*s*. 8*d*., being due to the growth of the Journal by 346 pages. Actually, the cost per page of the Journal is 5*d*. less this year than last, being £1 15*s*. 6*d*. for 1926 and £1 15*s*. 11*d*. for 1925. Other causes of the increased expenditure are to be found in an advance in the cost of the Annual Reports of £107 4*s*. 2*d*., due to an increase in the size of the volume which, it is believed, will not recur, and in the expense entailed by the superannuation scheme, namely £176 5*s*. 2*d*. on behalf of the general staff and £88 15*s*. on behalf of the Library staff, which the Society has had to meet for the first time this year. The items under "House Expenses and Repairs" and "Furniture" show an increase of £116 9*s*. 11*d*. This has been caused by the need for providing new floor coverings for the inner library (tea-room), for the office, and for the redecoration and relighting of the Council Room; it has also been necessary to provide the office with additional furniture. Nevertheless, despite this extra expenditure, the general administrative expenses have increased by only £8 0*s*. 9*d*. owing mainly to the exercise of economy in other directions and to the transference of part of the expenses to the Library Account.

The general financial position of the Society could, therefore, be regarded as satisfactory were it not for the fact that it is evident, from the increase in the volume of chemical publications both this year and last, that the curve representing the world's annual output of new chemical knowledge is still rising. A steadily increasing expenditure due to this cause cannot be met by the establishment of any capital fund, because it is clear that such a fund would have to be augmented by some £5000 yearly to be of any service. It can only be met by providing new income in other ways, and, in this connexion, it must be remembered that during the past five years the ordinary annual income of the Society has been increased by £3594, or, in other words, that the income for 1926 is greater by that amount than the income for 1921. This has been accomplished without raising the subscription, and, in consequence, there are now not many new sources of income that can be made available. A few years will show whether this increase in material which must be published is normal and recurrent, for, if it should prove to be so, the Council will have to consider in what way the situation can be met.

Library Account. In order to present a more complete picture of the annual cost of the Library and of the manner in which the participating Societies contribute towards its maintenance, the account has, this year, been printed as a separate item, in which the superannuation charges of the Library staff and a proper proportion of the general overhead administrative charges are included. For these reasons the item of £2093 11*s.* 6*d.*, for Library Expenses, appearing in the General Income and Expenditure Account as against £1799 2*s.* 3*d.* for last year, does not wholly represent an increase in the cost of the Library, because the difference includes superannuation charges and general expenses (amounting to £215 9*s.* 11*d.*), the latter of which has hitherto been included in the General Account.

Publications Fund. The capital of the Fund now stands at £7170 3*s.* 9*d.* The donations for the year amount to £1102 9*s.*, and the subscriptions to £85 18*s.* The sum of £1500 has been invested during the year, and with this £491 7*s.* 0*d.* Five per cent. War Stock and £1310 5*s.* 5*d.* Three and a half per cent. Conversion Stock have been purchased. In addition, the Society received £1800 Five per cent. War Stock transferred at par from the Pedler estate, so that the sum invested on the Publications Fund Account has been increased by £3300. The Fund has contributed £761 16*s.* 2*d.* towards the cost of the Society's publications, but £350 of this was derived from the Government Publication Grant of the Royal Society, for which the Council desires to express its acknowledgment and thanks. Life composition fees amounting to £190 10*s.* have been transferred to the Capital Account. It is a matter for regret that further delays occurred in distributing the estate of the late Sir Alexander Pedler. However, at a meeting of representatives of the four Societies concerned under the Will, a scheme of distribution was agreed on, the negotiations being placed in the hands of Messrs. W. B. Keen and Co. The final distribution of the estate was made early in 1927, too late to be included in the present accounts, and in future the Publications Fund Account will benefit by the full amount of interest accruing each year from the Pedler Bequest.

Special Publications Fund. In response to a request frequently made for photographs of Chemists, it was decided to publish, as an experiment, portraits of the following eight Chemists: R. W. Bunsen, Emil Fischer, A. W. von Hofmann, D. I. Mendeléeff, Louis Pasteur, Sir William Perkin, Sir William Ramsay, and Sir Henry E. Roscoe. There is a steady demand for these portraits, which are reproduced by a photolithographic process, and the venture is being financed by the Special Publications Fund Account. The cost of these portraits was £171 14*s*. 10*d*., and already £72 3*s*. 11*d*. has been obtained by their sale. The sale of the Memorial Lectures, Vol. I., has realised £43 2*s*., making, with the amount received last year, a sum of £95 12*s*. towards the original cost of £225 3*s*.

Staff Superannuation Scheme. The decision of the Council, made last year, to establish a staff superannuation scheme on a contributory basis has this year, as mentioned elsewhere, caused an increase in the ordinary expenditure of £176 5*s*. 2*d*. on behalf of the general staff and of £88 15*s*. in respect of the Library. During the year, £159 12*s*. has been contributed by Fellows to the Staff Pensions Fund, and this, together with the sum of £200 transferred during the year from the General Fund, has brought the capital of the Fund to £377 15*s*. 11*d*. The Council wishes to thank those Fellows who have contributed to the Fund, but desires to emphasise the need for further donations in order that the Fund may serve the purpose for which it has been established. The sum of £51 15*s*. has been paid out in pensions during the year.

Sales of Publications. As a result of the increased price charged to the public for the Abstracts in Pure Chemistry for 1926, the income received from this source has been increased by £371 12*s*. 4*d*. There is, however, a decrease in the amount received from the sale of the Journal of £32 3*s*. 1*d*. The sale of the Annual Reports realised £767 1*s*. 11*d*., as against £759 3*s*. 3*d*. last year, and it is evident that in the present circumstances the Council cannot afford to relinquish any part of this important source of income by remitting the charge which Fellows have at present to pay for this publication.

A vote of thanks to the Auditors (Prof. A. J. Allmand, Prof. J. S. S. Brame and Dr. G. W. Monier-Williams), proposed by the TREASURER and seconded by Dr. P. C. AUSTIN, was carried, acknowledgment being made by Dr. G. W. MONIER-WILLIAMS.

It was moved from the Chair and carried unanimously that Drs. O. L. Brady, A. E. Dunstan, and G. W. Monier-Williams be elected Auditors for the coming year.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council and Committees for their services during the past year was proposed by Dr. J. A. VOELCKER, seconded by Prof. A. FINDLAY, and carried unanimously, response being made by Prof. J. C. PHILIP.

In presenting the Longstaff Medal for 1927 to Prof. R. Robinson, the PRESIDENT stated:

"PROFESSOR ROBINSON,

"The award which I am about to make is the highest distinction which the Chemical Society can bestow on one of its Fellows, and the Council believes that the present award will meet with the cordial approval of all the Fellows of the Society.

"Your investigations of the chemistry of the alkaloids have not only elucidated the structure of some of these extremely complicated substances but have also indicated in a striking manner the possible mechanism of the processes by which they may be formed in Nature. You have also achieved outstanding success in your inquiries into the constitution and synthesis of the colouring matters of flowers and in your studies of the mechanism of reactions in Organic Chemistry. All this work has secured for you a place in the foremost rank of Organic Chemists and you have conferred distinction on British Chemistry.

"It is with the very greatest pleasure that I now award you the Longstaff Medal, and, on behalf of the Council and Fellows, express the hope that your work in the future will be crowned with even greater success than it has been in the past."

THE PRESIDENT said that it had been found possible to make the first award of the Harrison Memorial Prize under the terms of the Trust Deed and that the Prize for 1926 had been awarded to Dr. Charles R. Harington. In making the presentation, the PRESIDENT said:

"DR. HARINGTON,

"The Harrison Memorial Prize is given for conspicuously meritorious work in any branch of chemistry pure or applied, and is regarded as an exceptional distinction to commemorate Edward Frank Harrison.

"Your ably conducted investigations have led to a greatly improved method for separating the pure hormone from the thyroid gland and finally to the synthesis of thyroxine indistinguishable chemically and physiologically from the natural thyroxine. This work constitutes such a notable contribution to chemical knowledge that the Selection Committee is justified in awarding you the Prize for 1926 in accordance with the terms of the Trust Deed.

"On behalf of the Harrison Memoria Prize Selection Committee, I award you the Harrison Memorial Prize and express the hope that your future work will be even more successful than that which you have already accomplished."

The President then delivered his address entitled:—"Experiments on Molecular Complexity." A vote of thanks to the President for his services in the Chair during the past year, and for his address, with the request that he would allow the Address to be printed in the Journal, was proposed by Prof. W. P. Wynne, seconded by Prof. A. Lapworth, and carried with acclamation, the President making acknowledgment with thanks.

The report on the election to vacancies on the Council for the year 1927—1928 was read as follows:

President.—H. Brereton Baker.

Vice-Presidents who have filled the office of President.—H. E. Armstrong, H. B. Dixon, Percy F. Frankland, Alexander Scott, W. P. Wynne.

Vice-Presidents who have not filled the office of President.—J. B. Cohen, G. G. Henderson, Sir Robert Robertson, R. Robinson, N. V. Sidgwick, Arthur Smithells.

Treasurer.—Jocelyn F. Thorpe.

Secretaries.—T. Slater Price, C. S. Gibson.

Foreign Secretary.—F. G. Donnan.

Ordinary Members of Council.—M. P. Applebey, H. Bassett, E. R. Bolton, H. V. A. Briscoe, J. E. Coates, J. C. Drummond, F. A. Freeth, F. W. Gamble, R. Whytlaw-Gray, J. Kenyon, T. J. Nolan, K. J. P. Orton, R. H. Pickard, B. D. Porritt, E. K. Rideal, J. F. Spencer, G. Stubbs, F. J. Wilson.

INCOME AND EXPENDITURE ACCOUNT

1925		*Income.*	1926	
£ s. d.	£ s. d.		£ s. d.	£ s. d.
	123 0 0	To Life Compositions		190 10 0
		,, Annual Subscriptions :—		
1083 0 0		Received in advance, on account of 1926	1054 10 0	
8130 0 0		,, during 1926 ,, ,, ...	8318 10 0	
446 8 0		,, ,, ,, ,, 1925	497 12 0	
16 10 0		,, ,, ,, ,, 1924 and previous years	89 8 0	
9675 18 0			9910 0 0	
500 0 0		*Less* amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	500 0 0	
9175 18 0			9410 0 0	
500 0 0	9675 18 0	*Add* Arrears at date: £886 8s.; Estimated to realise as per Balance Sheet	500 0 0	9910 0 0
		,, Investments, Dividends on :—		
24 11 11		£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	25 3 10	
35 18 8		£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock, 1914/54	36 10 0	
35 0 0		£1400 India 2½ per cent. Stock	35 0 0	
48 0 0		£2400 Bristol Corporation 2½ per cent. Debenture Stock	48 0 0	
84 15 7		£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	86 16 4	
28 7 0		£1200 Leeds Corporation 3 per cent. Stock	28 16 0	
45 0 0		£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53 ...	45 0 0	
28 2 6		£1200 London and North Eastern Railway 3 per cent. Debenture Stock	28 16 0	
19 5 10		£700 Canada 3½ per cent. Stock, 1930/50	19 12 0	
105 0 0		£2100 5 per cent. War Stock, 1929/47	105 0 0	
44 0 0		£1100 5 per cent. War Bonds, 1929/47	44 0 0	
24 0 0		£600 Funding Loan, 4 per cent., 1960/90	24 0 0	
374 0 0		£11873 3½ per cent. Conversion Stock	332 9 0	
137 5 3		,, Income Tax Recovered	114 0 0	
51 4 11	1084 11 8	,, Interest on Deposit	55 7 10	1028 11
		,, Publication Sales :—		
2663 11 0		Journals and Proceedings	2631 7 11	
2067 0 7		Abstracts	2438 12 11	
64 4 6		Collective Index, Vols. I–VI	113 10 4	
759 3 3		Annual Reports on Progress of Chemistry	767 1 11	
22 0 0		Berichte	—	
—		Memorial Lectures. Vol. II.	27 9 0	
—		Other Publications	9 4	
5575 19 4			5978 11 5	
513 19 9	5061 19 7	*Less* Publishers' Commission	546 9 9	5432 1 8
596 17 0		,, Proceeds of Advertisements in Journal and Abstracts ...	538 1 5	
57 11 8	539 5 4	*Less* Commission	148 1 9	389 19 8
	25 10 9	,, Miscellaneous Receipts...		30 2 11
	681 15 0	,, Donations to Library		682 16 0
	28 17 6	,, Subscriptions from other Societies		29 18 6
		,, Transfer from Publications Fund, viz. :—		
350 0 0		Government Publications Grant (through the Royal Society)	350 0 0	
184 3 4		Dividends and Interest on Deposit	325 18 2	
88 10 6	622 13 10	Subscriptions	85 18 0	761 16 2
	£17,843 11 8			£18,455 15 11
	80 0 0	To Pedler Bequest, Income from Residue of Estate of Sir Alexander Pedler		143 19 4
	—	,, Pedler Bequest, on Account of Capital		1800 0 0
	—	,, Excess of extraordinary Expenditure over extraordinary Income, carried to Balance Sheet		421 0 0
	£80 0 0			£2,364 19 4

FOR THE YEAR ENDED 31ST DECEMBER, 1926.

1925		*Expenditure.*	1926	
£ s. d.	£ s. d.		£ s. d.	£ s. d.
		By Expenses on account of Journal:—		
869 0 0		Editorial Salaries	995 7 0	
69 10 7		Editorial Postages	68 5 1	
3428 15 1		Printing of Journal	3673 7 1	
69 7 5		Banding	88 11 4	
128 17 8		Printing of Advertisements	78 12 7	
5 14 1		Addressograph Labels	5 9 9	
474 9 5		Distribution of Journal	510 7 11	
312 8 9		Authors' Copies	336 14 3	
5 5 0		Insurance of Stock	5 5 0	
5 10 2		Warehousing of Stock	17 11	
—		Miscellaneous	11 16 11	
	5363 18 2			5769 14 10
		,, Expenses on account of Abstracts:—		
1085 0 0		Editorial Salaries	1150 15 0	
34 10 0		Editorial Postages	39 16 11	
1287 11 11		Abstractors' Fees	1194 11 6	
3026 8 10		Printing of Abstracts	3073 5 3	
69 7 4		Banding	88 11 4	
5 14 2		Addressograph Labels	5 9 8	
474 9 5		Distribution of Abstracts	510 8 0	
5 5 0		Insurance of Stock	5 5 0	
5 10 2		Warehousing of Stock	17 10	
61 17 2		Miscellaneous	55 15 11	
	6055 14 0			6124 16 5
	27 11 6	,, Lecture Expenses		36 14 8
	84 17 8	,, Advance Proofs and Reports of Meetings		90 12 7
	528 15 1	Annual Reports on the Progress of Chemistry		635 19 [illegible]
	13 18 10	Purchase of Back Numbers of Publications		40 8 10
	126 2 0	List of Fellows—Printing, etc.		
	1799 2 3	Library Expenses		2093 11 6
		,, Donations:—		
100 0 0		Annual Tables of Constants	—	
50 0 0		British Empire Exhibition	—	
—		Optical Conventions	10 10 0	
—		Federal Council	100 0 0	
	150 0 0			110 10 0
		,, Administration Expenses:—		
1427 12 9		Salaries of Staff	1436 13 6	
414 6 0		Wages (Commissionaire, Housekeeper, and Charwomen	412 14 6	
16 5 0		Pensions	—	
83 12 1		Coal and Lighting	57 4 1	
109 16 3		House Expenses and Repairs	153 2 10	
—		Furniture	78 3 4	
22 0 2		Telephone	22 16 0	
43 0 3		Tea Expenses	34 4 7	
25 0 4		Insurances	24 16 4	
31 10 0		Accountants' Charges	31 10 0	
6 17 3		Commission on Recovery of Income Tax	5 14 0	
472 3 7		Miscellaneous Printing and Stationery	446 16 0	
201 13 1		Postages	155 6 8	
10 10 0		Legal Charges	—	
—		Expenses at Annual General Meeting at Manchester	85 0 7	
16 7 11		Carriage on Journals to Germany	—	
16 0 0		New Press and Renovating Seal	—	
14 14 0		Addresses	19 2 0	
80 8 3		Miscellaneous Expenses	91 13 8	
	2091 16 11			2999 17 8
		,, Superannuation of Staff		*176 5 2
	123 0 0	,, Transfer to Publications Fund (Life Composition Fees)		190 10 0
	112 11 5	,, Collective Index Vol. VI		—
		,, Staff Pensions Fund—Pensions paid during 1926		51 15 0
	466 4 3	,, Excess of ordinary Income over ordinary Expenditure carried to Balance Sheet		135 0 0
	£17,843 11 8			£18,455 15 11
	80 0 0	By Publications Fund—Income from Pedler Bequest		143 19 4
	—	,, Publications Fund—Capital from Pedler Bequest		1800 0 0
	—	,, Staff Pensions Fund, transferred from accumulation of General Purposes Account at 31st December, 1925		200 0
	—	,, Cost of New Library Bookshelves		221 0
	£80 0 0			£2,364 19 4

* A further £88 15s. 0d. is included in Library Expenses.

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1926.

RESEARCH FUND.

1925 £ s. d.	*Income.*	1926 £ s. d.	1926 £ s. d.
	To Dividends on:		
31 5 0	£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock ...	32 0 0	
20 3 11	£1034 Great Western Railway 2½ per cent. Stock	20 13 8	
34 5 8	£1142 16s. New South Wales 3 per cent. Stock	34 5 8	
33 13 2	£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2	
26 13 1	£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	27 5 10	
19 0 10	£806 Victoria 3 per cent. Stock, 1929/49	19 6 10	
224 18 6	£4498 11s. 0d. 5% War Loan, 1929/47 ...	224 18 6	
192 7 0	£5164 13s. 9d. 3½% Conversion Stock ...	180 15 2	572 18 10
50 17 4	,, Income Tax Recovered		27 0 0
111 5 8	,, Repayment of Grants		180 15 0
4 17 0	,, Interest on Deposit		15 19 6
—	,, Sale of Apparatus		31 16 5
17 11 8	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		—
£766 18 10			£828 9 9

1925 £ s. d.	*Expenditure.*	1926 £ s. d.	1926 £ s. d.
758 10 0	By Grants		772 0 0
2 10 10	,, Commission on Recovery of Income Tax...		1 7 0
5 18 0	,, Advertisements, etc.		6 19 0
—	,, Honorarium to Lecturer		21 0 0
—	,, Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...		27 3 9
£766 18 10			£828 9 9

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

1925		1926	1926
	To Dividends on:—		
25 0 0	£500 National War Bonds, 5%, 1928 ...	25 0 0	
25 0 0	£500 National War Bonds 5%, 1929 ...	25 0 0	
2 3 2	£61 15s. 8d. Conversion Stock, 3½% ...	2 3 2	
4 9 7	Interest on Deposit	3 9 2	55 12 4
—	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		84 12 2
£56 12 9			£140 4 6

1925		1926	1926
2 4 6	By Advertisements		5 4 6
—	,, Cost of Plaque..		135 0 0
54 8 3	,, Balance, being excess of Income over Expenditure, carried to Balance Sheet		—
£56 12 9			£140 4 6

PUBLICATIONS FUND.

1925 £ s. d.	*Income.*	1926 £ s. d.
123 0 0	To Transfer from General Account, being Life Composition Fees for year...	190 10 0
101 0 6	,, Subscriptions ...	99 0 0
2395 14 4	,, Donations ...	1102 9 0
20 19 2	,, Interest on Deposit ...	4 19 0
350 0 0	,, Government Publications Grant (through the Royal Society) ...	350 0 0
83 4 2	,, Dividend on £5,933 10s. 2d. Conversion Stock, 3½ per cent. ...	152 8 6
—	,, Dividend on £491 17s. War Stock, 5%, 1929/47	24 11 4
—	,, Income Tax recovered ...	9 4 8
£3073 18 2		£1933 2 6
	To Transfer from General Purposes Account.	
80 0 0	Income from Pedler Bequest ...	143 19 4
—	,, Ditto on account of Capital ...	1800 0 0
£80 0 0		£1943 19 4

1925 £ s. d.	*Expenditure.*	1926 £ s. d.	1926 £ s. d.
	By Transfer to General Account—Income applicable to 1926 Publications, viz.:—		
350 0 0	,, Government Publications Grant (through the Royal Society) ...	350 0 0	
184 3 4	,, Dividends and Interest on Deposit ...	325 18 2	
88 10 6	,, Subscriptions ...	85 18 0	761 16 2
—	,, Commission on recovery of Income Tax ...		9 3
12 10 0	,, Subscriptions in advance ...		13 2 0
2438 14 4	,, Balance, being excess of ord. Income over ord. Expenditure, carried to Balance Sheet		1157 15 1
£3073 18 2			£1933 2 6
80 0 0	By Balance, being excess of extraordinary Income over extraordinary Expenditure carried to Balance Sheet ...		1943 19 4
£80 0 0			£1943 19 4

SPECIAL PUBLICATIONS FUND.

1925 £ s. d.	*Income.*	1926 £ s. d.	1926 £ s. d.
	To Sales:—		
52 10 0	Memorial Lectures, Vol. I ...	43 2 0	
—	Portraits ...	72 3 11	
		115 5 11	
	Less Commission ...	4 16 11	110 9 0
—	,, Dividend on £2115 8s. 10d. Conv. Stock, 3½%		59 4 8
—	,, Interest on Deposit...		9
172 13 0	,, Balance, being Excess of Expenditure over Income carried to Balance Sheet ...		19 8 1
£225 3 0			£189 2 6

1925 £ s. d.	*Expenditure.*	1926 £ s. d.
	By Cost of Reproduction:—	
225 3 0	Memorial Lectures, Vol. I ...	—
—	Printing Portraits of Eminent Chemists	171 14 10
—	,, Advertising ...	17 6 6
—	,, Miscellaneous Expenses ...	1 2
£225 3 0		£189 2 6

STAFF PENSIONS FUND.

1925 £ s. d.	*Income.*	1926 £ s. d.
15 15 0	To Subscriptions ...	—
—	,, Transfer from General Account (from accumulation of Funds) ...	200 0 0
—	,, Ditto from General Account (to meet pensions for current year) ...	51 15 0
—	,, Donations...	159 12 0
—	,, Interest on Deposit...	2 8 11
£15 15 0		£413 15 11

1925 £ s. d.	*Expenditure.*	1926 £ s. d.
—	By Pensions paid during 1926 ...	51 15 0
15 15	,, Excess of Income over Expenditure carried to Balance Sheet ...	362 0 11
£15 15 0		£413 15 11

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1926.

LIBRARY.

1925 £ s. d.	*Income.*	1926 £ s. d.	£ s. d.
	To Donations:—		
250 0 0	Association of British Chemical Manufacturers		250 0 0
10 10 0	Biochemical Society		10 10 0
5 5 0	Faraday Society		5 5 0
45 0 0	Institute of Brewing		45 0 0
250 0 0	Institute of Chemistry		250 0 0
100 0 0	Society of Chemical Industry		100 0 0
10 0 0	Society of Dyers and Colourists		10 10 0
10 10 0	Society of Public Analysts		10 10 0
—	Jones, J. P.		1 1 0
—	„ Contribution from General Fund		1410 15 6
			£2093 11 6

1925 £ s. d.	*Expenditure.*	1926 £ s. d.	£ s. d.
1185 10 0	By Salaries		1222 17 6
—	„ Superannuation of Staff		88 15 0
483 7 6	„ Books and Periodicals		526 11 4
130 4 9	„ Binding		128 12 9
	„ Printing, Stationery and Postage		42 2 4
	„ Lighting, Heating, Furniture, etc.		79 7 4
	„ Miscellaneous		5 5 3
			£2093 11 6

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31ST DECEMBER, 1926.

GENERAL PURPOSES.

1925 £ s. d.	*Liabilities.*	£ s. d.	£ s. d.
1060 10 0	To Subs. received in advance:— at £3 0 0 ...		942 0 0
2905 2 6	„ Sundry Creditors (Printing and other Expenses)		2221 10 7
—	„ Bankers—overdraft		464 9 8
25,660 6 5	„ Excess of Assets over Liabilities as per last Balance Sheet	26,126 10 8	
466 4 3	*Add* Excess of Income over Expenditure for Year	135 0 0	
		26,261 10 8	
—	*Less* Excess of extraordinary Expenditure over extraordinary Income for Year	421 0 0	25,840 10 8
£30,092 3 2			£29,468 10 11

1925 £ s. d.	*Assets.*	£ s. d.	£ s. d.
	By Investments (value when acquired):—		
839 3 7	£787 London, Midland and Scottish Railway 4 cent. Debenture Stock ...	839 3 7	
1650 0 0	£1520 14*s.* 3*d.* Cardiff Corpn. 3% Stock	1650 0 0	
1316 1 0	£1400 India 2½ per cent Stock	1316 1 0	
2070 2 0	£2400 Bristol Corpn. 2½% Debenture Stock, Bristol Dock Account	2070 2 0	
3572 0 4	£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4	
1143 1 0	£1200 Leeds Corporation 3% Stock ...	1143 1 0	
1460 13 6	£1500 Transvaal 3 per cent. Guaranteed Stock, 1923–53	1460 13 6	
1033 11 0	£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1033 11 0	
704 8 6	£700 Canada 3½% Stock, 1930/50 ...	704 8 6	
1995 0 0	£2100 5 per cent. War Stock, 1929/47...	1995 0 0	
1045 0 2	£1100 5% National War Bonds, 1929/47	1045 0 2	
480 0 0	£600 4 per cent. Funding Loan, 1960/90	480 0 0	
8987 2 2	£11,873 3½ per cent. Conversion Stock (Market Value £21,807 16*s.* 2*d.*)	8987 2 2	26,296 3 3
2593 18 10	„ Sundry Debtors...		2617 19 9
500 0 0	„ Subscriptions in Arrear £386 8*s.* Estimated to realise		500 0 0
52 9 3	„ Insurance paid in advance		47 7 0
1 13 6	„ Cash in Hand		7 0 11
647 18 4	„ Cash at Bank		—
£30,092 3 2			£29,468 10 11

RESEARCH FUND.

1925 £ s. d.		1926 £ s. d.	1926 £ s. d.
14,462 4 2	To Excess of Assets over Liabilities as per last Balance Sheet	14,444 12 6	
—	*Add* Excess of Income over Expenditure for Year	27 3 9	14,471 16 3
17 11 8	*Less* Excess of Expenditure over Income for Year		—
£14,444 12 6			£14,471 16 3

1925 £ s. d.		1926 £ s. d.	1926 £ s. d.
	By Investments (value when acquired):		
1010 0 0	£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0	
1049 15 11	£1034 Gt. West. Rly. 2½% Debentures	1049 15 11	
1000 0 0	£1142 16*s.* 0*d.* New South Wales 3 per cent. Stock 1935	1000 0 0	
1002 16 9	£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
1009 18 9	£853 London, Midland and Scottish Railway 4% Debenture Stock ...	1009 18 9	
706 6 2	£806 Victoria 3% Stock, 1929/49 ...	706 6 2	
4267 4 10	£4498 11*s.* 0*d.* 5% War Stock, 1929/47	4267 4 10	
3898 14 10	£5164 13*s.* 9*d.* 3½% Conversion Stock (Market Value £12,576 7*s.* 9*d.*)	3898 14 10	13,944 17 3
99 15 3	,, Cash at Bank ... Current Account	26 19 0	
400 0 0	Do. ... Deposit Account	500 0 0	526 19 0
£14,444 12 6			£14,471 16 3

THE EDWARD FRANK HARRISON MEMORIAL TRUST

1925 £ s. d.		1926 £ s. d.	1926 £ s. d.
1251 6 8	To Excess of Assets over Liabilities as per last Balance Sheet	1305 14 11	
—	*Less* Excess of Expenditure over Income for Year	84 12 2	1221 2 9
54 8 3	*Add* Excess of Income over Expenditure for Year		—
£1305 14 11			£1221 2 9

1925 £ s. d.		1926 £ s. d.	1926 £ s. d.
	By Investments (value when acquired):—		
500 0 0	£500 National War Bonds 5 per cent. 1928	500 0 0	
500 0 0	£500 National War Bonds 5 per cent. 1929	500 0 0	
50 1 5	£61 15*s.* 8*d.* 3½ per cent. Conversion Stock (Market Value £1099 6*s.* 0*d.*)	50 1 5	1050 1 5
55 13 6	Cash at Bank ... ... Current Account	71 1 4	
200 0 0	Do. ... ... Deposit Account	100 0 0	171 1 4
£1305 14 11			£1221 2 9

PUBLICATIONS FUND

1925 £ s. d.		1926 £ s. d.	1926 £ s. d.
12 10 0	To Subscriptions received in advance ...		13 2 0
1536 13 0	,, Excess of Assets over Liabilities as per last Balance Sheet	4055 7 4	
2518 14 4	*Add* Excess of ordinary Income over ordinary Expenditure for Year	1157 15 1	
—	,, Excess of extraordinary Income over extraordinary Expenditure for year	1943 19 4	7157 1 9
£4067 17 4			£7170 3 9

1925 £ s. d.		1926 £ s. d.	1926 £ s. d.
	By Investments (value when acquired):—		
3500 0 0	£5938 10*s.* 2*d.* 3½% Conversion Stock ...	4500 0 0	
—	£2291 7*s.* 0*d.* 5% War Loan 1929/47 ... (Market Value £6806 0*s.* 6*d.*)	2300 0 0	6800 0 0
18 0 0	,, Life Composition Fee		—
549 17 4	,, Cash at Bank		370 3 9
£4067 17 4			£7170 3 9

SPECIAL PUBLICATIONS FUND

1925 £ s. d.	*Liabilities.*	1926 £ s. d	£ s. d.
	To Excess of Assets over Liabilities as per		
1896 8 4	last Balance Sheet	1723 15 4	—
	Less Excess of Expenditure over Income to 31st December, 1926	19 8 1	1704 7 3
£1723 15 4			£1704 7 3

1925 £ s. d.	*Assets.*	1926 £ s. d	£ s. d.
	By Investment:—		
1600 0 0	£2115 8s. 10d. 3½% Conversion Stock ... (Market Value £1602 16s. 8d.)		1600 0 0
45 15 0	,, Sundry Debtors for Sales (Less Commission)		43 12 6
78 0 4	,, Cash at Bank ... ... Current Account	10 14 9	
	Do. ... ... Deposit Account	50 0 0	60 14 9
£1723 15 4			£1704 7 3

STAFF PENSIONS FUND

1925 £ s. d.	*Liabilities.*	1926 £ s. d	£ s. d.
15 15 0	To Excess of Income over Expenditure		—
—	,, Excess of Assets over Liabilities as per last Balance Sheet	15 15 0	
—	*Add* Excess of Income over Expenditure for year...	362 0 11	377 15 11
£15 15 0			£377 15 11

1925 £ s. d.	*Assets.*	1926 £ s. d	£ s. d.
—	By Investment £371 17s. 1d. War Stock 5% 1929/47 (Market Value £375 2s. 1d.) ...		375 0 0
15 15 0	,, Cash at Bank		15 11
£15 15 0			£377 15 11

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

28, QUEEN VICTORIA STREET, E.C. 4.
February 9th, 1927.

Approved { J. S. S. BRAME,
A. J. ALLMAND,
G. W. MONIER-WILLIAMS

PRESIDENTIAL ADDRESS.

Delivered at the Annual General Meeting, March 24th, 1927.

By H. Brereton Baker, C.B.E., D.Sc., F.R.S.

Experiments on Molecular Association.

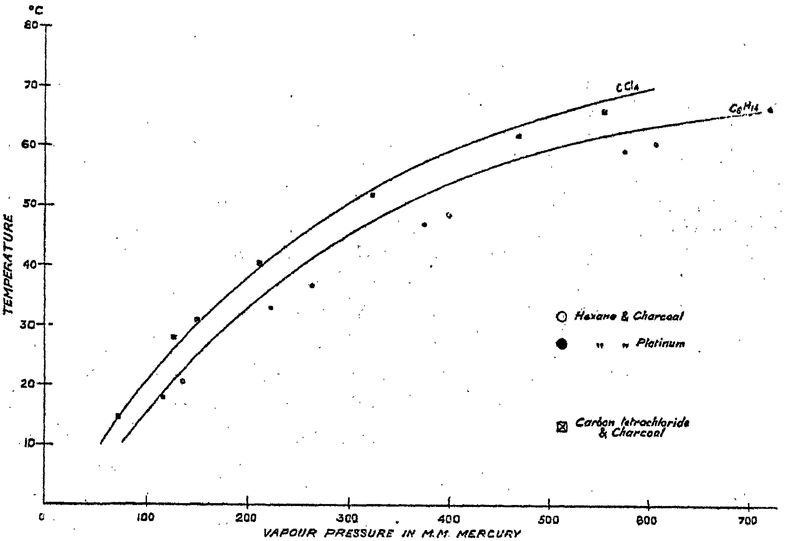
The molecular constitution of liquids has been the subject of much investigation. It is known that in acetic acid we have molecules which have double the simple formula, and that this complex is stable even when the liquid is converted into vapour. In water, the association is even greater than this at low temperatures, but the larger molecules are less stable and can scarcely persist when the liquid is vaporised. Bromine shows some evidence of association in the vapour, but owing to experimental difficulties, little is known as to the constitution of the liquid. On the other hand, liquids such as benzene and the lower-boiling paraffins have been considered as containing only the simplest molecules. It was shown, however, some five years ago that if liquids of very diverse types were subjected to prolonged drying, the boiling points were raised to a considerable extent. This is ascribed to the increase in complexity of the molecules when the catalyst, water, is removed. Since this rise of boiling point has been shown to take place both with benzene and with hexane, two typically unassociated liquids, it is probable that, instead of associated liquids being exceptional, all liquids may be capable of association. It is supposed that there is a continual combination and dissociation of the molecules in an ordinary liquid. It is known that water can promote, not only chemical combination, but also dissociation. If water is removed as completely as possible, its absence might conceivably work in two directions: the molecular equilibrium might be reached when the molecules were much more complex owing to absence of dissociation, or, in a liquid which was normally associated, the molecules might be much less complex owing to their inability, in absence of water, to combine together. The latter state has not yet been attained; we have not been able to obtain dry liquids which boil at a lower temperature than the normal. It is true that in the very fruitful week when Prof. Smits was working with me in my laboratory, dried benzene was fractionally distilled and the first fraction which came over boiled at 80°, leaving the higher-boiling fraction (118°) behind. If instead of benzene, which is normally associated only to a small extent, we had been dealing with bromine, which is much more associated in its normal condition, it is possible that we should have been able to distil off a fraction boiling below 59°.

It was with the hope of throwing some light on this question of the equilibrium of complex and simple molecules in a liquid that a new series of experiments was undertaken, with the object of finding out if catalysts other than water had a disturbing influence. I wish to acknowledge here the invaluable help given in their performance by my assistant, Miss M. Carlton.

Two main methods of attack on the problem were chosen, the determination of the vapour pressure and the measurement of surface tension.

In the first series of experiments on vapour pressures, charcoal was used as the catalyst. Barometer tubes were made of hard Jena glass, one end of which dipped under mercury. The upper ends were furnished with bulbs in which very pure sugar charcoal could be heated to redness while the tube was being exhausted. After admission of the liquid, the tube connecting the bulb with the pump was sealed off and the tubes were surrounded by a jacket of circulating water.

FIG. 1.



The continuous curves are the normal vapour pressure–temperature curves.

The results of these preliminary experiments left no doubt as to the influence of the presence of charcoal on the vapour pressure. With ether at 16°, the vapour pressure was 25 mm. greater than with the liquid alone. With methyl alcohol at 18°, the vapour pressure was 6 mm., and at 35° 12 mm., greater in the presence of the catalyst. With benzene, the increase with the charcoal was

2 mm. only, and this excess of vapour pressure was unaltered whether the temperature was 23° or 37°.

It was found, however, that quantitative measurements of the vapour pressures of each of the liquids showed considerable variations and a lengthy series of experiments was made using the two methods devised by Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, 32, 907, 1412). Some of the results are given in Fig. 1. These experiments again failed to give results which were concordant when the same liquid and the same catalyst were used in successive experiments. They did, however, lead to two important conclusions. We had ascribed our failure to obtain concordant results in the first series to the difficulty of obtaining the catalysts in the same condition of activity; different methods of treatment, different temperatures of treatment, and even age alone might have influenced their catalytic power.

The first fact which became clear in these preliminary experiments was that a catalyst in a liquid acts very slowly and sometimes at first even in a contrary direction to that shown in the final equilibrium. That is, in any liquid there is a balance between the large and the small molecules, for in all the liquids, ten in number, which we have examined there is evidence of some association. The presence of certain catalysts can influence the equilibrium, under different temperature conditions, in the direction of producing more complex molecules and so lowering the vapour pressure, and then, under different conditions, especially long time of contact, may produce increased dissociation and higher vapour pressure.

The second difficulty was caused by the fact that a pure liquid appears to have no constancy in its composition. For instance, pure bromine, without any catalyst, gave vapour pressures which showed considerable variations according to the history of the particular specimen. If bromine were boiled for some time and the measurement taken as soon afterwards as possible, it was found that the vapour pressure was very sensibly higher than it had been before the boiling took place. The recovery of the old vapour pressure was quite slow and many days elapsed before the effect of the boiling had disappeared.

In order to eliminate the effect of this change in the liquid alone, the next series of experiments was designed. In them the vapour pressure of the liquid was balanced against the pressure of the liquid with the catalyst, through a pressure gauge. The form of the apparatus is seen in Fig. 2.

To each of the upper ends of a U-shaped tube containing mercury was sealed a pair of bulbs, which were connected with each other by a capillary tube. Into one bulb was introduced the catalyst, and the liquid was placed in the second of the pair. The same liquid was then introduced into one of the bulbs of the other pair, the second one being left empty. All the entrance tubes but one were sealed off. The remaining tube was connected to a Hyvac pump. The liquid in the two bulbs was allowed to boil in the evacuated space in order to get rid of dissolved air: the liquid was then frozen and thereafter the bulb containing the catalyst was suitably heated with the same object. The tube connected with the pump was now sealed off, and the apparatus allowed to stand for an hour. Finally, the capillary tube connecting the two sets of bulbs was sealed with a fine-pointed flame. On transferring the apparatus to a thermostat it was found that the mercury level was the same in both limbs of the U-tube, showing that the apparatus was in order. By cooling the bulb containing the catalyst, the liquid was distilled over from the adjoining bulb. In this way, the two lots of liquid could be treated in exactly the same way, and a direct determination could be made of the difference in vapour pressure brought about by the catalyst. The results are in the table on p. 953.

Fig. 3.

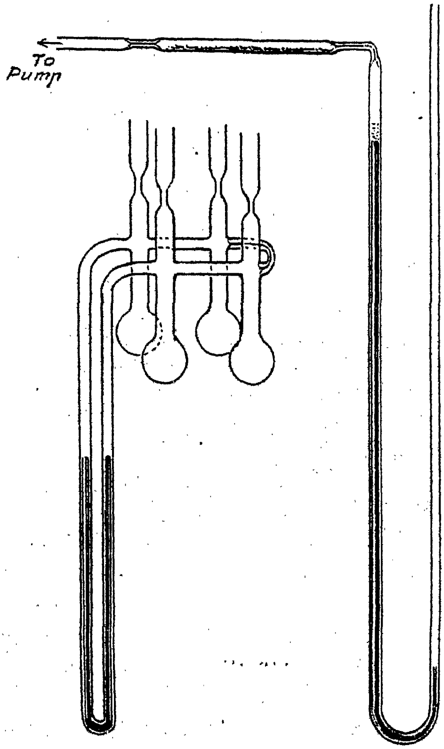


Fig. 2.

In each of the systems investigated there was an increase in the vapour pressure of the liquid in contact with the catalyst over the vapour pressure of the liquid alone. This difference increased with time up to a certain point and then became constant. The effect of the increase of vapour pressure produced by a catalyst was always seen with this apparatus, for, on standing, the liquid evaporated away from the catalyst and condensed in another part of the apparatus, although the whole was kept at a constant temperature in a thermostat.

The effects of heating and of cooling on this difference of vapour pressure were investigated and it was found that heating increased the difference and cooling diminished it. On standing, however, the original value of the difference was restored, although in some cases the time needed was some weeks.

Acetic acid and charcoal.

Time.	Diff. in mm. Hg.
Day of sealing	2·15
2 Days later ...	1·5
After heating at 80° for 4 hrs....	2·95
6 Days later ...	2·0
After keeping at 15° for 24 hrs.	2·05
2 Days later ...	2·4
5 Months later	1·9

Acetic acid and platinum black.

Time.	Diff. in mm. Hg.
Day of sealing	0·3
1 Day later ...	0·25
After heating at 80° for 4 hrs....	0·5
1 Day later......	0·75
6 Days later ...	0·8
After cooling at 15° for 1 day	1·05
3 Days later ...	1·6
After heating at 90° for 4 hrs.	1·75
5 Months later	2·2

Acetic acid and thoria.

Time.	Diff. in mm. Hg.
Day of sealing	0·4
3 Weeks later...	0·25
3 Weeks later....	1·27
Heated at 90° for 4 hrs.	1·32

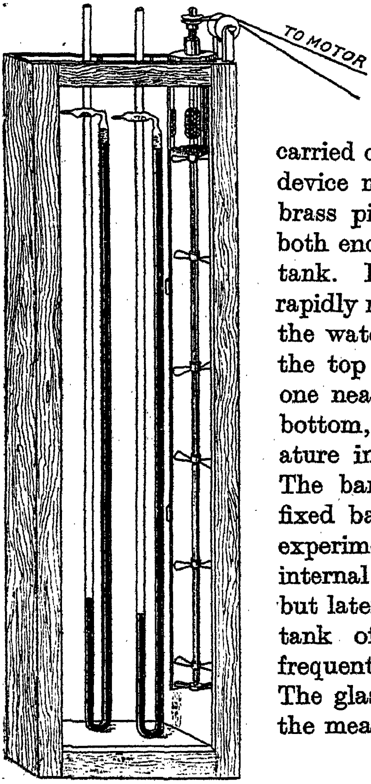
Benzene and nickel. Diff. in mm. Hg.	Methyl alcohol and charcoal. Diff. in mm. Hg.	Ether and charcoal. Diff. in mm. Hg.
3·4	5·5	40·0
3·3	6·3	41·3
3·3	6·2	41·2
3·5	6·5	39·2
3·1	6·1	40·2

Bromine and charcoal.

Time.	Diff. in mm. H_2SO_4 satd. with bromine.	Time.	Diff. in mm. H_2SO_4 satd. with bromine.
—	38·5	Interval of 2 days ...	95·2
Interval of 2 days ...	50·9	Interval of 14 days ...	125·1
Interval of 1 day	51·7	Interval of 16 days ...	133·75
Interval of 1 day	52·8	Interval of 3 days ...	142·3
Interval of 6 days ...	85·2		

In order to investigate the effect of heating on the vapour pressure of the liquid alone as well as in presence of catalysts, a return was made to the barometer tube method, with greatly improved apparatus (Fig. 3). The tube was U-shaped and made of Jena glass. The upper end of one limb was bent into a horizontal position, and by drawing it out to a capillary a bulb was formed, about 2 inches in length, to hold the catalyst. The liquid was introduced into the main barometer tube, and the catalyst into its bulb. The tube was then exhausted through the capillary and, after the liquid had been allowed to boil to expel dissolved air, the part of the vertical tube containing it was frozen and the catalyst was heated. As it was found difficult to obtain charcoal in the same state of activity in successive experiments, it was necessary to give this substance the same heat treatment. This was accomplished by slipping over the horizontal bulb a small electric furnace which maintained the charcoal at 450° for 1½ hours, the pump being kept running during the whole period. The capillary tube was then sealed, and the tube transferred to a large thermostat (Fig. 4). This was 1 sq. ft. in section and 3 ft. 6 in. in height. It was built of heavy teak, with thick plate-glass windows on opposite sides. It was filled with water and the stirring was carried out most effectively by an ingenious device made by Mr. W. J. Colebrook. A brass pipe, 5 inches in diameter, open at both ends, extends the whole height of the tank. In it is a screw propeller which, rapidly rotated by an electric motor, pumps the water continually from the bottom to the top of the tank. Two thermometers, one near the top and the other near the bottom, indicate the constancy of temperature in the different parts of the tank. The barometer tubes were clamped to a fixed bar inside the tank. In the earlier experiments, heating was effected by an internal coil carrying superheated steam, but later this was carried on in a separate tank of galvanised iron, owing to the frequent fracture of the glass windows. The glass-fronted thermostat was kept for the measurements alone.

FIG. 4.



Acetic Acid.

Catalyst.	Before heating.	Heated at 80° for 24 hrs., then cooled to 20°.	One week after heating at 20°.
None.	Normal.	+2 mm.	Normal.
Charcoal.	+1·8 mm. After an interval of 6 weeks, +6·0 mm.	+2·3 mm	+6·8 mm.
Thoria.	+0·65 mm. After an interval of 6 weeks, +7·3 mm.	+1·5 mm.	+7·3 mm.
Platinum.	+2·72 mm. After an interval of 6 weeks, −1·2 mm.	−3·8 mm.	+1·1 mm.

Water.

Catalyst.	Before heating.	Heated at 80° for 48 hrs., then cooled to 20°.	Two weeks after, at 20°.
None.	Normal.	Normal.	Normal.
Charcoal.	+2·5 mm.	+4·3 mm. 1 Day later, +0·75 mm.	+2·5 mm.
Thoria.	+2·4 mm.	+4·0 mm. 1 Day later, +1·2 mm.	+0·9 mm.
Platinum.	+1 mm.	+3·2 mm. 1 Day later, +0·6 mm.	+0·5 mm.

Measurements of the vapour pressure of water in the presence of the catalysts charcoal, platinum, and thoria show that in each instance heating has the same ultimate effect, but the interval between the actual heating and the appearance of the effect of the heating varies with the different catalysts. With thoria and platinum, heating at 80° for 24 hours produces an increase in vapour pressure, at the ordinary temperature, but if the time of heating be prolonged to 48 hours the vapour pressure within 24 hours of the heating shows a decrease from the constant value, this decrease disappearing if the tubes be allowed to stand for a few days at room temperature.

The charcoal and water, when heated at 80° for 24 hours, shows an increase in vapour pressure, if the readings be made within 24 hours of the heating; but two days after the heating the value of the vapour pressure diminishes and becomes less than before heating. This low value slowly changes back to the constant value when the barometer tubes containing the water and charcoal are allowed to stand at the ordinary temperature for a few days.

With acetic acid, charcoal as catalyst produces a decrease after 24 hours' heating; after 72 hours' heating, there is a decrease which temporarily increases for a day or two, the normal value finally returning. Thoria causes a decrease in vapour pressure when heated with acetic acid, the amount of the decrease being greatest a day or two after the heating has taken place. With platinum, a diminution in vapour pressure is caused by heating, the normal value returning after a short while.

Surface Tension Measurements.

The vapour pressure determinations having shown that the presence of catalysts produces a change in liquids, experiments were undertaken to find the molecular weights of some liquids by the method of Ramsay and Shields. Although the absolute accuracy of this method has been disputed, the differences we have found between the molecular weights of liquids alone and in the presence of catalysts are so marked that any small deviations from the true values are probably unimportant.

The determinations of the diameters of the capillary tubes were made with a microscope, kindly lent by Professor Fowler, which reads directly to the 1/1000th of a millimetre. These capillaries were sealed to glass sinkers and cleaned with a mixture of nitric and chromic acids. The containing tubes were made of special resistant glass, the formula of which was worked out by myself and the late Mr. H. J. Powell, of the Whitefriars Glass Works. The liquids were shown to have taken up no weighable amounts either from the glass or from the catalyst even after a year's contact.

The measurements were taken in a large thermostat provided with an electrically driven stirrer. Half an hour before the heights of the liquids in the capillaries were measured, the tubes were taken out and tilted to see that the liquids ran freely in the capillaries. There was always a danger that the finely powdered catalyst might block the minute opening at the bottom of the capillary. The catalysts and the liquids used were from the same preparations as those which were used in the vapour pressure experiments.

The study of surface tension was directed chiefly to the effect of three catalysts—pure charcoal, platinum black, and oxide of thorium—on the three liquids water, acetic acid, and bromine.

In all cases, comparative tubes were used containing the liquid alone, without the presence of any catalyst, so that a direct estimation of the effect of the catalyst could be made under various conditions of temperature, etc.

It has been found that the catalyst does not seem to produce its maximum effect on the complexity of the molecules at once. This is seen by the following table: the temperature interval was about 20°, the higher temperature being 40°.

Acetic Acid and Charcoal.

	Time.	Mol. wt.
After	1 day	1·541 × 60
,,	2 days	1·952 × 60
,,	3 weeks	2·525 × 60
,,	12 months	2·492 × 60

Acetic Acid alone.

	Time.	Mol. wt.
After	1 day	1·546 × 60
,,	2 days	1·568 × 60
,,	3 weeks	2·097 × 60
,,	9 months	2·097 × 60

Acetic Acid and Platinum Black.

	Time.	Mol. wt.
After	2 weeks	2·40 × 60
,,	3 months	2·273 × 60
,,	8 months	2·976 × 60

Acetic Acid and Thoria.

	Time.	Mol. wt.
After	1 day	2·538 × 60

The table for acetic acid alone shows that the acid does not reach its normal value in 2 days after filling. This points to the conclusion that in the process of filling the tube, which involves the boiling of the liquid for some time to get rid of air, dissociation of the molecules of liquid takes place, and that in 3 weeks the normal molecular weight is restored. With charcoal the same phenomenon is observed, but the molecular weight is greater by 24. With platinum black, the molecular weight is greater by 52, whilst with thoria the increase in molecular weight due to the catalyst is 29.

A similar effect is seen with water and the same catalysts.

Water and Platinum.

Time.	Mol. wt.
Day of filling	3·352 × 18
After 6 months	4·442 × 18
Heated at 40° for 16 hrs.	3·948 × 18
1 Week later	3·713 × 18
2 Weeks later	3·047 × 18
1 Day later	2·915 × 18

Water and Thoria.

Time.	Mol. wt.
3 Weeks after filling ...	3·125 × 18
5 Weeks after filling ...	3·612 × 18
9 Weeks after filling ...	3·866 × 18

Ramsay and Shields' value for this temperature interval is 3·259 × 18.

This method, as used, appears to have a disadvantage because the heating, even to only 40°, seems to disturb the equilibrium and this is not restored at once on cooling to the ordinary temperature. It was therefore decided to make a study of the effect of temperature on the constitution of these liquids in presence and in absence of catalysts. It must be pointed out that, after heating or cooling, the liquids were allowed to stand at the ordinary temperature for the time specified, so that the effects shown are those not measured at the high or low temperature, but through the usual interval 17—40°.

Acetic Acid.

Catalyst.	Before heating.	After heating at 80° for 2 hrs.	After heating at 80° for 48 hrs.	After 24 hrs. at the ordinary temperature.
None	2·168 × 60	2·32 × 60	1·97 × 60	1·666 × 60
Platinum black	1·872 × 60	2·527 × 60	1·782 × 60	1·586 × 60
Charcoal	2·492 × 60	2·552 × 60	1·690 × 60	2·490 × 60
Thoria	1·992 × 60	2·538 × 60	2·218 × 60	2·452 × 60

Attention may be directed, not only to the effect of the catalysts on the complexity of the molecules of the different liquids, but also to the different effects of heating for various lengths of time. Except in the cases of bromine alone and of charcoal in acetic acid, heating for only a short period seems to increase the molecular complexity, whilst heating for a long period decreases it, as would be expected. The recovery to normal is slow, but even after 3 days' standing at the ordinary temperature the molecular weight is often considerably above or below that at the beginning of the experiments.

The agreement between the vapour-pressure and the surface-tension results is not quantitative. This could not be expected, since, by the surface tension method the *average* complexity of the molecules is estimated, whilst the vapour pressure measured will be, very largely at all events, that of the smaller molecules present.

The view of the constitution of liquids which is indicated by these experiments is that all liquids may be regarded as analogous to a dissociable gas such as nitrogen tetroxide. At low temperatures the heavy molecules are more numerous; at higher temperatures the lighter ones predominate, and dissociation and combination are probably both increasing. Liquids differ, however, in this respect, that dissociation and association are much slower in liquids than in gases. Equilibrium in liquids may be profoundly disturbed by even a comparatively slight change of temperature, and complete recovery of the normal condition may be a question of weeks or even months.

The effect of the presence of a solid catalyst is, as would be expected, produced much more slowly in a liquid than in a gas, and it is not easy to understand how the catalyst comes to exert its special influence. All one can say at present is that this influence is exerted in the case of all the liquids on which experiments have been made.

OBITUARY NOTICE.

JOSEPH JOHN ACWORTH.

BORN 1853; DIED JANUARY 3RD, 1927.

DR. ACWORTH was born at Rochester in 1853 and died on January 3, 1927, aged 73. He was elected a Fellow of this Society on March 4, 1875, so that he had more than completed his Jubilee of fellowship. He was admitted a Fellow of the Institute of Chemistry in 1878, that is, the year after the Institute was founded.

Acworth was from his boyhood interested in experimental science, and after working in the Chemical Laboratories of the Royal College of Chemistry at South Kensington, he communicated a paper to this Society " On the Action of Nitric Acid upon Copper, Mercury, etc., and on the Influence of the Presence of Metallic Nitrates," which was published in the *Journal* for 1875. He appears to have continued working at this subject at the London Institution with Prof. H. E. Armstrong, and a paper in their joint names was published in the *Journal* two years later, " Researches on the Reduction of Nitric Acid and the Oxides of Nitrogen. Part I. On the Gases evolved by the Action of Metals on Nitric Acid." After this he passed to what proved to be his life work, namely, the manufacture of photographic sensitive materials. It was in quite the early days of the gelatine dry plate industry that he spent a few years in the laboratories of the Britannia Dry Plate Company (now the Ilford Company), and leaving there went to the University of Erlangen to work for the Ph.D. degree in Wiedemann's laboratories. His thesis was presented in May, 1890, and printed (*Ann. Phys. Chem.*, 1891, pp. 371—406) in 1891, " On the Relation between Absorption and Sensitiveness of Sensitised Plates," chiefly plates that had been sensitised for colour by dyes. A translation of the essential parts of this paper appeared in the *Photographic Quarterly* for April, 1891. Acworth was back again in England in 1890 (aged 37), and built a factory at Cricklewood for the manufacture of gelatine dry plates, and in March, 1892, the "Imperial" plates were advertised for sale. These works under his personal guidance, both technically and commercially, were probably the most prosperous of any in the country. Ill health led him to dispose of his interests in the company about the year 1917 (*Brit. Journ. Phot.*).

Eastman, in 1889, introduced commercially his transparent rollable film, the base being nitrocellulose. In 1890, Acworth was granted a patent for a film base of gelatine rendered waterproof by passing it through a solution of nitrocellulose. This method does not appear to have been followed up. From 1892 to 1896, inclusive, he made four communications to the Royal Photographic Society and one to the Camera Club, which will be found in the respective Journals. In his technical work, he was very capably assisted by his wife, who, as Miss Marion Whiteford Stevenson, had taken the Associateship course at the Royal College of Science and received her diploma (A.R.C.Sc.) in physics in 1893. She was the third woman to earn the Associateship, and the first in physics.

Acworth was of a very kindly and genial nature, and he was in no sense "spoiled" by either his prosperity or his afflictions. He suffered for very many years from asthma and other troubles apparently associated with it. This may have tended to increase his inborn nervous and retiring disposition. Those who heard him on the few occasions when he spoke in public would hardly realise how distressing it was to him to do so, for he had the necessary strength of will and power of perseverance to succeed. C. J.

CXXXIV.—*Studies in the Fenchene Series. Part I. A Synthesis of* apo*Fenchocamphoric Acid.*

By WALLACE FRANK SHORT.

APART from the syntheses of *l*-β- and *d*-α-fenchene from nopinolacetic acid by Wallach (*Annalen*, 1907, **357**, 82; 1908, **363**, 1) and of *r*-fenchone by Ruzicka (*Ber.*, 1917, **50**, 1362), a *complete* synthesis has not yet been effected in the fenchene series. In order to achieve this, a favourable starting-point would appear to be *apo*fenchocamphoric acid. Hitherto this acid has been obtained from camphenilane by oxidation with nitric acid (Nametkin and Chuchrikovaia, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 425; Nametkin and Michailovna, *ibid.*, 1917, **49**, 417) and, in almost theoretical yield, from β-fenchocamphorone by oxidation with potassium permanganate (Komppa and Roschiev, *Ann. Acad. Sci. Fennicae*, 1917, *A*, **15**, 1; Roschiev, *ibid.*, 1919, *A*, **10**, 1; Komppa and Roschiev, *Annalen*, 1922, **429**, 175; Nametkin, *ibid.*, 1924, **438**, 185). It is regarded as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid; this structure, however, has not been definitely established (compare Roberts, *J. Amer. Chem. Soc.*, 1926, **48**, 1975). The acid has now been synthesised by the condensation of *iso*butylene dibromide with ethyl disodiopropane-ααγγ-tetracarboxylate according to the classical methods of the Perkin school. The yield is very small owing to loss of bromine from the *iso*butylene dibromide with formation of *iso*butylene, α-bromo*iso*butylene, and other compounds, and is, moreover, adversely affected by slight variations in the conditions of preparation. Loss of hydrogen bromide was anticipated from the observations of other investigators (Bentley, J., 1895, **67**, 266), but the loss of both bromine atoms was somewhat unexpected, since Otto and Mühle (*J. pr. Chem.*, 1895, **51**, 519) state that *iso*butylene dibromide is attacked by sodium only with difficulty.

Although the synthesis is uneconomical, it establishes the constitution of *apo*fenchocamphoric acid as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid.

EXPERIMENTAL.

Ethyl propane-ααγγ-tetracarboxylate (b. p. 194—195°/11 mm.) (88·5 g.; 1 mol.) and 130 c.c. of toluene were shaken with 9·2 g. (1½ atoms) of powdered sodium until this dissolved; 43·2 g. (¾ mol.) of *iso*butylene dibromide (b.p. 36—37°/10 mm.; Taboury, *Bull. Soc. chim.*, 1911, **9**, 125) were then added and the mixture was boiled for 60 hours. *iso*Butylene was steadily evolved and sodium bromide deposited. The product was poured into water and the oil so obtained was distilled under 10 mm. pressure. After removal of the substances boiling below 194°, there remained a small quantity of a thick syrup. This was boiled for 3 hours with 3 g. of potassium hydroxide dissolved in alcohol. The acid obtained on acidification, m. p. 170—179° (decomp.), was heated at 220—230° until the evolution of carbon dioxide had ceased. The semi-solid residue was washed twice with 10 c.c. of water, which extracted a small quantity of glutaric acid. The dried residue, m. p. 110—115°, was treated with 6 g. of acetyl chloride for 2 days, the excess of the latter then removed at 60° under reduced pressure, and the residue was shaken with 11 c.c. of cold 5% caustic soda solution, washed with water, dried, and recrystallised from benzene–light petroleum. It melted at 136—137°, and by solution in hot 10% caustic soda solution and reprecipitation with sulphuric acid, 0·6 g. of an acid (m. p. 143—145°) was obtained (*cis-apo*fenchocamphoric acid melts at 144·5—145°). From the acidified 5% caustic soda extract, crystals (1·3 g.) were deposited which melted at 147—148° after recrystallisation from ether (Found : C, 58·2; H, 7·6 by the micro-Pregl method; equiv., 93·6. Calc. for $C_9H_{14}O_4$: C, 58·1; H, 7·5%; equiv., 93·0). *trans-apo*Fenchocamphoric acid melts at 147—148° (Nametkin, *Annalen*, 1924, **438**, 185). The total yield of *apo*fenchocamphoric acid was 1·9 g. or 5% of the theoretical.

The author is indebted to the Chemical Society for a grant which partly defrayed the cost of this research, and to Prof. J. K. H. Inglis for an arrangement which prevented overlapping.

UNIVERSITY COLLEGE, AUCKLAND,
NEW ZEALAND.

[*Received, December 7th,* 1926.]

CXXXV.—*The Action of Nitric Acid on Acetylene and Ethylene.*

By PHYLLIS VIOLET McKIE.

IT has been shown (Orton and McKie, J., 1920, **117**, 283) that the principal products of the interaction of fuming nitric acid with acetylene are carbon dioxide and trinitromethane. In the reaction between fuming nitric acid and ethylene a similar formation occurs, but prior to the production of trinitromethane the addition compound, β-nitroethyl alcohol, is formed.

It is now possible to formulate a course of reaction between nitric acid and an ethylenic or acetylenic compound. From the presence in the products of (*a*) β-nitroethyl alcohol (from ethylene) and (*b*) nitrolic acids, and the direct formation of nitroparaffins from these compounds, it is deduced that the primary reaction is one of addition of hydroxyl and the nitro-group to the unsaturated linking, forming the nitro-alcohol. This, in the case of acetylene, becomes by further addition the unstable dinitrodihydroxy-compound. Oxidation and reaction with nitrous acid gives the corresponding nitrolic acid, together with carbon dioxide, from which trinitromethane is finally derived. Such a reaction is entirely in harmony with the reaction between oxides of nitrogen and unsaturated linkings (Schmidt, *Ber.*, 1901, **34**, 3536; 1902, **35**, 2323) and with the addition of nitric acid to various unsaturated compounds (Wieland and Rahn, *Ber.*, 1921, **54**, 1770; Cohn, *Ber.*, 1891, **24**, 3865).

The following equations represent the probable courses of reaction :

Acetylene : $CH{\vdots}CH \longrightarrow CH(OH){:}CH(NO_2) \longrightarrow [CH(OH)_2{\cdot}CH(NO_2)_2]$
$\longrightarrow CH(NO_2)_2{\cdot}CHO \longrightarrow CH(NO_2)_2{\cdot}CO_2H \longrightarrow CH_2(NO_2)_2 + CO_2$
$CH_2(NO_2)_2 \longrightarrow C(NO_2)_2{:}N{\cdot}OH \longrightarrow CH(NO_2)_3$

Ethylene : $CH_2{:}CH_2 \longrightarrow CH_2(OH){\cdot}CH_2(NO_2) \longrightarrow CH_2(NO_2){\cdot}CHO$
$\longrightarrow CH_2(NO_2){\cdot}CO_2H \longrightarrow CH_3{\cdot}NO_2 \longrightarrow CH(NO_2){:}N{\cdot}OH$
$\longrightarrow CH_2(NO_2)_2 \longrightarrow C(NO_2)_2{:}NOH \longrightarrow CH(NO_2)_3$.

EXPERIMENTAL.

Dry ethylene (97—99% purity), prepared by the vaporisation of ethyl alcohol in an iron combustion tube packed with pumice stone soaked in syrupy phosphoric acid and heated to 250—300°, was passed into fuming nitric acid diluted to various concentrations. The experimental procedure was in all respects similar to that used for acetylene (Orton and McKie, *loc. cit.*). The absorption of ethylene by concentrated nitric acid is rather less ready than is that of acetylene, and there is a markedly lower evolution of carbon dioxide. The ratio Carbon dioxide evolved/Ethylene absorbed is, for 95% nitric acid, 0·4 : 1; whereas the ratio Carbon dioxide evolved/Acetylene absorbed is 0·8 : 1; in the presence of mercury salts, however, these ratios show a closer approximation. The yield of tetranitromethane obtained by further nitration of the product (Orton and McKie, *loc. cit.*), expressed as a percentage of the hydrocarbon absorbed, in the ethylene reaction never rises to, and is often much less than, the value obtained for acetylene, and no variation of experimental conditions has altered this relation. The maximum yield of tetranitromethane in one operation in the absence of a catalyst is obtained by the absorption of 2·7—2·9 l. of acetylene or of 2·9—3·1 l. of ethylene by 100 g. of 95% nitric acid. The yield of tetranitromethane is 9—10 g. (from acetylene), or 277% of the acetylene absorbed, or 6—7 g. (from ethylene), or 231%. The addition of 0·66% of mercuric nitrate raises the value for ethylene to 332·9% (compare acetylene, 453—532%). Hence the amount of carbon in the ethylene reaction used up in side reactions is considerable, 30—40%, which can partly be accounted for by the formation of oxalic acid representing 28%.

TABLE I.

	Per 100 g. of HNO_3.		$C(NO_2)_4$ as percentage of C_2H_4 absorbed.	% C in C_2H_4 becoming		
% HNO_3.	C_2H_4 (l.) absorbed.	CO_2 (l.) evolved.		$C(NO_2)_4$.	CO_2.	other substances.
100	2·146	—	98·4			
97·5	3·100	—	116·2			
95·0	2·980	—	231·8			
95·0	2·764	2·504	204·3			
90·0	2·980	0·210	198·1			
90·0	2·846	0·451	201·4			
Compare acetylene :						
95·0	2·288	2·855	278·7			
0·33% Mercuric nitrate as catalyst.						
95·0	2·900	1·930	300·4	21·46	37·98	40·56
0·66% Mercuric nitrate as catalyst.						
95·0	3·044	2·453	332·9	23·78	40·3	35·92
Compare acetylene :						
95·0	3·02	4·39	383·0	29·2	70·8	0·0

TABLE II.

Relation between oxalic acid produced and hydrocarbon absorbed.

					% C becoming			
% HNO_3.	Hydrocarbon absorbed (l.).	CO_2 evolved (l.).	$H_2C_2O_4$ (g.).	$\frac{CO_2}{H_2C_3O_4}$ by wt.	CO_2.	$C(NO_2)_4$.	$H_2C_2O_4$.	Carbon unaccounted for.
Ethylene :								
95	3·152	2·699	2·774	1·93	42·5	25·34	21·61	10·55
90	1·484	0·608	1·710	0·71	20·49	29·8	28·34	21·37
Acetylene :								
95	3·792	3·212	2·357	2·69	42·15	17·42	15·29	25·14

Influence of Mercuric Nitrate.—Mercuric nitrate has, as in the reaction with acetylene, a favourable effect on the rate of absorption of ethylene and hence on the speed of interaction, and considerably increases the yield of nitroform. The effect of the mercury salt is complex, but is largely to prevent the alternative reaction of simple oxidation, thus increasing proportionally the addition reaction producing the nitro-alcohol. Side reactions are considerably reduced in its presence. A higher concentration of mercuric nitrate was required to produce the maximum absorption of ethylene and the maximum yield of tetranitromethane than in the case of acetylene, and 0·66% was found to promote the best results. The ratio of Carbon dioxide evolved/Ethylene absorbed approached unity under the optimum conditions, but exceeded it only in exceptional cases.

Isolation of β-*Nitroethyl Alcohol.*—The product of the reaction between ethylene and fuming nitric acid was diluted with water, neutralised with sodium carbonate, and extracted with ether. From the washed and dried extract, by fractional distillation under diminished pressure, β-nitroethyl alcohol was obtained as a faintly yellow oil, b. p. 117—121°/30—35 mm.

The amount of nitroform which can be extracted and estimated by the ordinary procedure is always in excess of the alcohol, the ratio of alcohol to nitroform being approximately 1 : 2·4. The presence of mercuric nitrate seems to have little effect on this ratio. If, however, the estimation of the two compounds be carried out before the completion of the reaction, this ratio is markedly different; the amount of nitroform which can be isolated at such stages is appreciably less than that at the end of the reaction, whereas the amount of nitro-alcohol is not. The ratio of the two substances when half the normal quantity of ethylene had been passed was unity. Two facts of importance emerge from these data. Nitroform is produced subsequently to and, it would appear, at the expense of the nitro-alcohol, and the formation of nitroform takes place largely towards the end of the passage of the hydrocarbon.

TABLE III.

Relation between β-nitroethyl alcohol and nitroform.

Experiment.	β-Nitroethyl alcohol (g.).	Nitroform (g.).	Nitro-alcohol/Nitroform
95% HNO_3. No Hg	1·98	4·6	1 : 2·32
95% HNO_3. Hg	4·59	11·4	1 : 2·48
95% HNO_3. No Hg	1·36	1·9	1 : 1·4
(½ ethylene passed)			
95% HNO_3. Hg	3·38	5·14	1 : 1·52

The author is indebted to the Chemical Society for a grant which partly defrayed the cost of this work.

BEDFORD COLLEGE, LONDON. [*Received, February* 15*th*, 1927.]

CXXXVI.—*The Production of Fog in the Neutralisation of Alkali with Hydrogen Halides.*

By Henry Oscar Askew.

When a current of air carrying phosgene (carbonyl chloride) is passed through charcoal and then bubbled through an aqueous-alcoholic solution of sodium hydroxide, a fog appears in the flask containing the alkali as soon as the charcoal is saturated with phosgene. This fog persists even when the air in which it is suspended is passed through another similar absorption vessel.* If the phosgene is replaced by phosphorus oxychloride, similar observations are made.

A preliminary investigation of this phenomenon soon showed that neither the phosgene nor the charcoal was essential, and that a fog was readily produced when a stream of air carrying hydrogen chloride was bubbled through an absorption flask containing an aqueous solution of sodium hydroxide. It was found, indeed, that the phosgene (or phosphorus oxychloride) was effective only by virtue of the hydrogen chloride arising from the hydrolysis by moisture in the charcoal (compare Bohart and Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 523). If a column of zinc dust (which absorbs hydrogen chloride but not phosgene) was interposed between the charcoal column and the absorption flask, the production of fog in the latter ceased. Further, if the charcoal was first freed from the greater part of its moisture by heating for some time at 160°, phosgene produced no fog under the original conditions.

Preliminary experiments also made it clear that the production of fog was not dependent on the presence of alcohol in the alkaline absorbent, although the presence of alcohol or other organic substances undoubtedly intensifies the fog. This matter is discussed in greater detail later.

The investigation accordingly resolved itself into a careful examination of (1) the conditions of bubbling under which this fog formation occurs, (2) the amount of fog and its dependence on the concentration of the alkali, (3) the effect of adding organic and colloid substances to the alkali, (4) the nature and concentration of the acid present in the fog particles, and (5) the size and possible electric charge of these particles.

EXPERIMENTAL.

As a source of hydrogen chloride concentrated hydrochloric acid was used. Two wash-bottles, W (Fig. 1), were placed in series in a thermostat at 25·0°, and purified air from the reservoir, R, under a pressure of about 18 inches of water (kept constant by the water valve, V), was passed through the acid. The mixed gases, after being dried and filtered through several cm. of woolly asbestos in which the thermometer, T_1, was placed, passed to the three-way tap, B, and thence through the jet, J, to the vessel, S, which contained the alkaline solution and was fitted with a ground glass head, H, and an outlet tube. The fog was filtered out of the air by woolly asbestos in the tube U_1, which was kept in a box packed with cotton wool. (Special tests showed that the air from which the fog had been filtered out was free from chloride.) The moist air then passed to the tubes U_2 and U_3 containing calcium chloride. The dry air passed to the manometer, M, through the vessel, E, and then to the aspirator, D. The levels of the liquid in the limbs of

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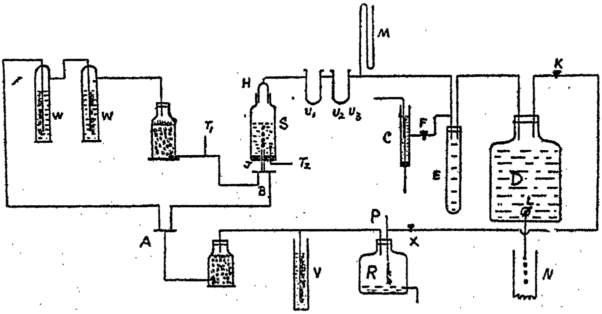
* The author's attention was directed to these facts by Prof. J. C. Philip.

FIG. 1.



M were kept the same throughout an experiment. In cases of difficulty in maintaining this setting, the constant-level arrangement, C, was set in operation by opening the tap, F, whereby, if the pressure shown by M was less than atmospheric, water entered the graduated vessel, E, until atmospheric pressure was restored; the volume of water entering E was deducted from that run out of the aspirator.

The graduated indicator card attached to the tap, L, on D allowed of duplicate settings being made, although in all cases exact check of the rate of outflow was kept by means of a stopwatch. The filter pump, P, was arranged so that it could be used for suction from the aspirator by opening the tap, K. When this was not desired, the air to be pumped into R entered through the inlet, X, on the pipe line. The thermometer, T_1, gave the temperature of the entering gas and T_2 that of the solution.

The various vessels, S, were of such sizes that, by always using the same volume of solution, the " depths " of liquid, as measured from the tip of the jet to the surface of the solution, were 7·5, 5·5, and 3·75 cm., respectively. Four jets were used, their radii being 1·81, 1·32, 1·08, and 0·82 mm., respectively. In order to prevent the solutions from creeping back into the barrels of the jets, the inside walls were coated with paraffin wax, but the tips were left clear.

All measurements of the rates of passage of the gas through the liquid are given in c.c. per minute. The alkali solutions were freed from carbonate, except where otherwise stated.

After the tube U_1 had been weighed, the asbestos was removed and extracted with water. The acidity as hydrogen chloride and the total chloride present were then estimated and invariably corresponded with one another. In the tables, "HCl %" refers to the percentage of acid by weight in the fog particles, both being given as mg. per litre of air. The standard quantity of air for an experiment was fixed at 2 l., as it was necessary to minimise the variation in concentration of the alkali.

Except where otherwise stated, the partial pressure of the hydrogen chloride is taken as 130 mm.

The amount of acid vapour which appears as fog varies between 0·8 and 12% of that passing through the jet, according to the solution used, the lower figure applying to simple aqueous solutions.

Conditions of Passage of Gas through the Solutions.—With aqueous solutions of sodium, potassium, and barium hydroxides an increase in the radius of the jet causes a greater production of fog, which, moreover, appears to attain a maximum at about 5·5 cm. depth, although, under similar conditions as to rate of passage, the amount of fog formed does not vary with depth by more than a few mg. per litre of air. In general, the concentration of acid in the particles is greatest when the depth of solution is 3·75 cm.

From Table I (giving mean values from 2 l. of gas), it will be seen that (1) the concentration of acid in the fog particles remains remarkably constant for a given jet; (2) the partial pressure of the water vapour in the air, after removal of the particles by the asbestos filter, is constant; and (3) increase in the rate of passage of the gas leads to an increase in the amount of fog. As the radius of the jet decreases and the depth of liquid increases, the relation between rate of passage and fog formation tends to become linear.

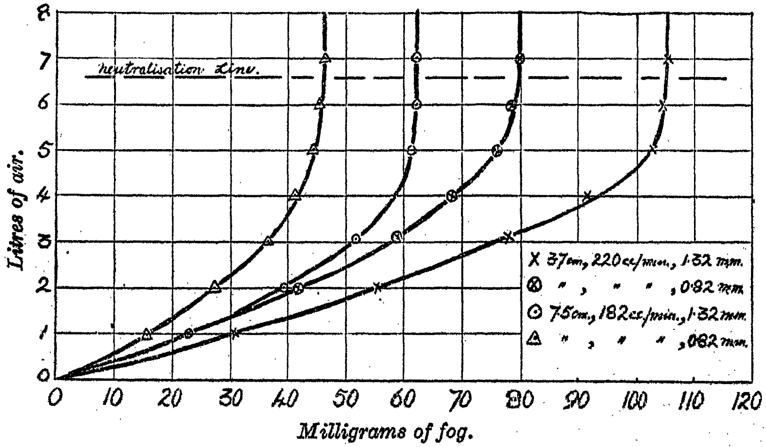
Concentration of Alkali.—Many experiments were made in which the same alkali solution was used until completely neutralised, the weight of fog formed being determined after each litre of air had been bubbled through the solution. As shown by Fig. 2 (for 0·614*N*-sodium hydroxide), the fog production falls off in every case as the alkali becomes weaker, and ceases when it is neutralised.

TABLE I.

Solution : 1·26*N*-NaOH. Depth : 7·5 cm. Air temp. : 20—23°.

Radius of jet, 1·81 mm.				Radius of jet, 1·32 mm.			
Rate (c.c./min.).	Fog (mg.).	HCl %.	Partial press. of H_2O (mm.).	Rate (c.c./min.).	Fog (mg.).	HCl %.	Partial press. o H_2O (mm.).
200	42·6	9·23	21·1	210	45·9	8·70	19·9
198	42·0	9·22	16·5	208	44·8	8·70	18·0
189	39·5	9·51	20·7	181	37·9	8·99	19·0
170	35·6	9·27	23·3	172	36·0	8·18	19·3
154	31·0	9·24	16·5	160	31·8	8·26	20·0
123	23·9	9·18	21·6	125	23·6	8·30	20·2
108	16·7	9·68	16·7	110	19·7	8·56	18·2

FIG. 2.



Solutions of potassium and barium hydroxides give similar results, although at corresponding concentrations less fog is obtained than with sodium hydroxide.

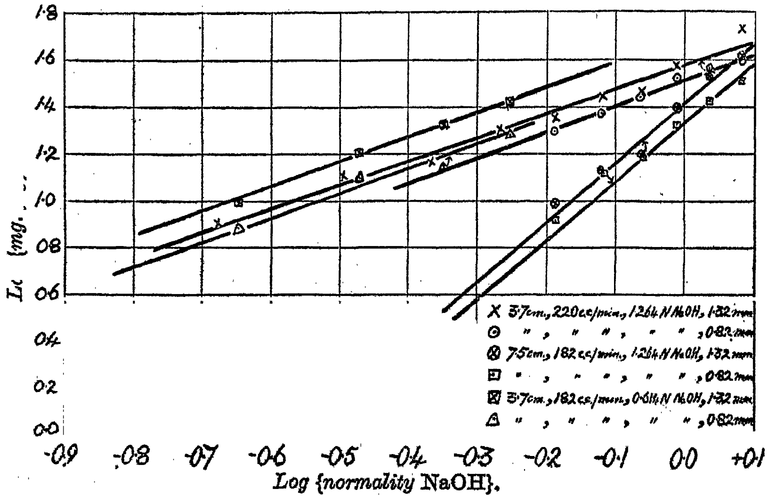
If the logarithm of the weight of fog obtained is plotted against that of the mean concentration of alkali during the passage of each litre of gas, a straight line is obtained. Moreover, under fixed conditions of depth and original concentration of alkali, the lines corresponding to the different jets are parallel, as shown in Fig. 3.

Table II shows the amount of fog formed at 20° (app.) in the first litre of air from different concentrations of sodium hydroxide (mean concentrations during each experiment). On plotting these figures it is seen that in dilute solutions the effect of the alkali is relatively great; in the more concentrated solutions, the amount of fog obtained is very nearly proportional to the alkali concentration.

TABLE II.

Depth of liquid (cm.).	Radius of jet (mm.).	Rate (c.c./min.).	Concentration. 0·07*N*.	0·26*N*.	0·56*N*.	1·21*N*.
3·7	1·32	220	14·0	22·2	30·9	49·2
		182	10·8	18·0	26·7	42·5
	0·82	220	9·9	16·4	22·8	39·4
		182	5·6	11·8	19·1	37·4
7·5	1·32	220	11·9	19·4	29·0	49·6
		182	9·6	15·6	22·8	40·7
	0·82	220	7·5	15·3	23·0	42·9
		182	4·8	8·6	15·8	32·4

FIG. 3.



In neutral or acid solutions of salts, dyes, and colloids (see later) and in water, in agreement with Fig. 2, all the hydrogen chloride is absorbed and no fogs are formed under the conditions of the present series of experiments. The incomplete absorption of the acid in alkaline solutions is not due to the rapid rates used, for in the presence of colloids and dyes thick fogs are obtained when only one bubble is formed every 2 or 3 seconds.

Solutions of the following salts of weak acids gave no fogs (in *N*-solution, except the diborate): Sodium acetate, sodium hydrogen carbonate, disodium hydrogen phosphate, sodium diborate (0·3*N*), and potassium dihydrogen phosphate. Thin fogs were formed with sodium carbonate and dense fogs with trisodium phosphate. The data in Table III were obtained for a depth of 7·5 cm. of solution, the rate being 225 c.c./min., the temperature 22°, and the jet radius 1·32 mm. They show clearly the changes in fog formation which

TABLE III.

Solution.	Air (l.).	Fog (mg.).	Solution.	Air (l.).	Fog (mg.).
N-Na_2CO_3.	1	9·7	N-Na_3PO_4.	1	25·5
	2	4·7		2	11·5
	3	4·1		3	1·3
	4	0·1		4	0·0

occur when the neutralisation has reached the hydrogen carbonate and disodium salt stages, respectively, and serve to emphasise the results of the foregoing experiments. Sodium carbonate is not so largely hydrolysed as trisodium phosphate and consequently its hydroxyl-ion concentration is somewhat less. This difference is plainly shown in the quantities of fog obtained. From the data in Table II, it is found that the concentrations of free sodium hydroxide which would give the same weight of fog under these conditions are $0{\cdot}06N$ and $0{\cdot}45N$, respectively; these are of the order of magnitude which would be expected from the degrees of hydrolysis. It has not been possible to fix a definite value for the hydroxyl-ion concentration at which fog formation begins, but it must be greater than $10^{-5}N$, since the other phosphates and sodium bicarbonate give no fog.

Addition of Organic and Colloidal Substances to the Alkali.—Ethyl alcohol, amyl alcohol, acetone, formaldehyde, and ether, especially when present in considerable amount, gave dense fogs, but no fog was obtained in the absence of alkali.

Experiments were made with the following "capillary-active" substances: *iso*Amyl alcohol, sucrose, gelatin, gum arabic, safranine, methylene-blue (hydrochloride), Congo-red, Orange G, glycerol, saponin, kaolin, aquadag, and purified clay. Solutions (or suspensions) of these substances in sodium hydroxide were made, and the fogs formed under different experimental conditions were investigated. As a typical example the results for gelatin solutions in $1{\cdot}24N$-sodium hydroxide are given in Table IV, which also

TABLE IV.

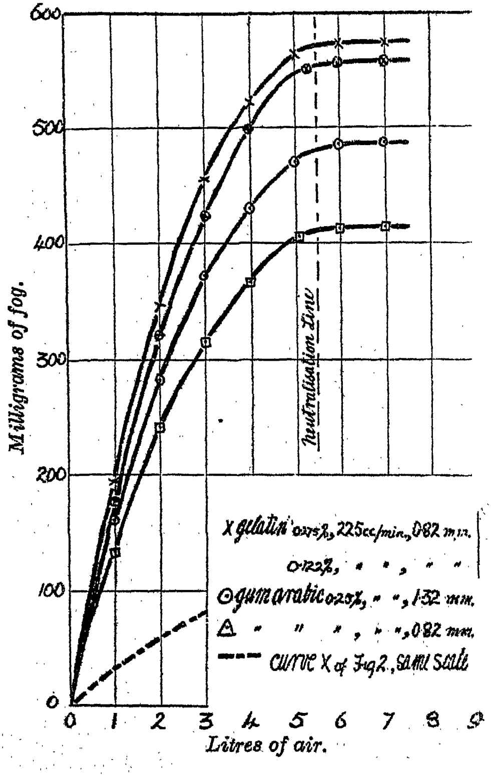
Rate: 208 c.c./min. Radius of jet: 1·32 mm. Depth: 7·5 cm.

Gelatin, %.	Fog (mg.).	Air temp.	Partial press. of H_2O (mm.).	Gelatin, %.	Fog (mg.).	Air temp.	Partial press. of H_2O (mm.).
0·0000	47·7	24·9°	21·7	0·041	141·4	25·8°	21·8
0·0032	63·0	25·3	21·9	0·081	153·8	25·1	22·2
0·0082	81·9	25·3	21·7	0·082	161·1	25·3	21·2
0·0163	102·9	25·7	22·3	0·098	167·3	23·9	19·7
0·041	137·7	24·5	22·3				

serves to show how constant and independent of the amount of fog formed is the aqueous vapour pressure of the air in contact with the particles.

In those cases where dense fogs are formed, the bubbles in passing up through the solutions become filled with fog and do not remain clear as in the case of the simple aqueous solutions. Addition of sodium chloride (0·5N) to the gelatin solutions caused a slight increase in the amount of fog formed, but small alterations in the concentration of the alkali did not have much effect. A peculiarity, which appears with other solutions also (see Fig. 5), was found with gelatin, *viz.*, that at about 110 c.c./min. the curve showing the relation between rate of passage of the gas and fog formation undergoes a sudden change of direction.

FIG. 4.



When the alkali solutions were treated with the air–hydrogen chloride mixture until neutralised, the concentration of acid in the particles was found to be practically independent of the stage of neutralisation. This was true, not only for gelatin but in general, for the other substances also.

As mentioned above, none of the solutions gave any fog after neutralisation. Comparison of the curves in Fig. 4 with those in Fig. 2 shows the great effect of adding colloidal substances to the solutions, and also the rapid decrease in fog formation as the solution becomes neutralised.

Safranine and methylene-blue were particularly active in fog formation. The pronounced effect of the latter, even in extremely dilute solutions, is shown in Table X. Sucrose, up to 5%, had no effect on fog formation; glycerol caused a decrease, probably owing to viscosity effects, as the solutions used were somewhat concentrated. All the other substances mentioned caused great increases in the amount of fog obtained.

When the data from which Fig. 4 was constructed were plotted in the same manner as used in Fig. 3, the curves were again linear. The slopes of these lines did not vary greatly with the capillary-active substance employed; thus, under corresponding conditions the lines for two solutions of differing gelatin content, for the gum arabic, and for the amyl alcohol solutions were almost parallel; with saponin, the results were somewhat irregular, but this is not surprising in view of the excessive formation of froth in this case. It will be seen later that, when the alkali concentration is kept constant and that of the added substance is varied, each substance has its own specific effect, *i.e.*, the slopes of the curves vary greatly according to the compound employed.

From the considerable amount of data obtained, it may be stated that: (1) The concentration of acid in the particles tends to decrease as that of the capillary-active substance decreases; *e.g.*, under similar conditions with a china clay in 0·343% and 0·206% suspensions, the concentrations of acid were, respectively, 8·32% and 7·83%, whilst in the case of methylene-blue a steady decrease in acidity occurred as the dye concentration decreased; (2) for a given concentration of capillary-active substance, the concentration of acid in the fog droplets is independent of that of the sodium hydroxide solutions, *e.g.*, with gelatin in 0·61*N*- and 1·24*N*-sodium hydroxide, the acid concentrations are the same for fogs formed under similar conditions; and (3) the partial pressure of aqueous vapour in the air surrounding the particles is constant and independent of the amount of fog formed.

Experiments with Hydrogen Bromide.—Hydrogen bromide, although much more active than the chloride, resembles it in giving no fog with water or with neutral or acidic salt solutions.

The experiments with colloids in 0·59*N*-sodium hydroxide solution (Table V) were carried out under the following conditions: Radius of jet, 1·32 mm.; rate, 208 c.c./min.; depth of liquid, 7·5 cm.; air temperature 21·0—21·8°.

TABLE V.

Colloid.	Air (l.).	Fog (mg.).	HBr, % (mean).	Part. press. of H_2O (mm.).
Gelatin (0·122%).	1	180·2	21·8	21·2
	2	164·1		22·0
	3	132·6		21·6
	4	106·3		20·1
Gum arabic (0·25%).	1	148·7	21·9	18·6
	2	133·5		20·6
	3	114·3		20·6
	4	89·7		20·4

The % of hydrogen bromide in the particles is very large, but constant whether colloids are present or not; expressed as normalities, however, the concentrations are nearly the same as (in fact, a little higher than) in the case of hydrogen chloride.

The relation between alkali concentration and fog formation is the same as for hydrogen chloride, and when plotted, the lines for gelatin and gum arabic are practically parallel.

The partial pressures (about 59 mm.) of the hydrogen bromide in the air and acid mixtures in these experiments were considerably lower than with hydrogen chloride, yet the amount of fog formed under similar conditions was greater; this is probably due to the slower diffusion of the hydrogen bromide.

Alcoholic Solutions.—The weaker solution used did not give very dense fogs, but the stronger gave very dense ones; in the latter case, the bubbles, as they passed up through the solution, were filled with fog. With strong alcoholic solutions, the narrower the jet the greater is the amount of fog obtained. This is the reverse of that found for the simple aqueous solutions.

The solutions contained 7·6% and 33·0% by weight of alcohol, respectively, and were 1·223*N* and 1·238*N* with regard to sodium hydroxide.

The alcohol in the fogs was estimated by Benedict and Norris's method (*J. Amer. Chem. Soc.*, 1898, 20, 293), in which a standard solution of potassium dichromate in concentrated sulphuric acid is used for oxidation, but since the presence of chloride in the solutions caused high results, the following modification was adopted. After extraction of the asbestos with water, the volume being kept as small as possible, the washings were run into a graduated flask to which an excess of 0·03185*N*-silver sulphate solution was added; after standing and being shaken for some time, the liquid was made up to volume. Portions were then filtered off for estimation of alcohol and of the excess silver. From the gross amount of alcohol found on analysis, a deduction was made for alcohol adsorbed by the asbestos, the latter having been determined by separate experiments.

An attempt was made to estimate separately the partial pressures of the alcohol and water vapours in the gas after filtering out the fog. Fresh calcium carbide, as described by Thomas (*J. Soc. Chem. Ind.*, 1922, 41, 33T), was used for this purpose. The change in weight of a U-tube filled with carbide multiplied by 2·91 (experimental factor determined by blank experiments) gave the weight of water vapour in a given volume of air; the alcohol was absorbed in concentrated sulphuric acid, which, as shown by blank experiments, did not absorb acetylene. Hence the partial pressures of the water and alcohol vapours could be calculated.

The fogs produced at each stage of the neutralisation of the stronger solution were analysed: the composition of the particles with regard to both alcohol and acid content remained constant.

Series of experiments similar to those already described for other solutions were carried out. As shown in Fig. 5, there is a critical rate below which the amount of fog formed falls off rapidly as the rate decreases. Some of the results are in Table VI. It is seen that the lower the alcohol concentration the greater is the % of acid in the fog particles. Moreover, the percentages of alcohol in the fog particles are somewhat greater than those in the original solution. In view of the work of Kablukow (*Z. physikal. Chem.*, 1903, **46**, 399), however, it is probable that the vapour given off by the alkaline solutions is richer in alcohol than that given off by a simple aqueous solution of the same alcohol content. If a correction is applied to the usual vapour-composition data, assuming that sodium hydroxide has the same effect on the vapour composition as potassium iodide, it is found that the % of alcohol to be expected in the liquid in equilibrium with that vapour is close to that actually found.

TABLE VI.

Solution: Aqueous alcohol, NaOH 1·23-*N*. Depth of liquid: 7·5 cm. Air temp.: 20·4—22·5°.

Alcohol, %.	Radius of jet (mm.).	Rate (c.c./min.).	Fog (mg./l. of air).	HCl, %.	Alcohol in fog, %.	Part. press. (mm.)	
						Alcohol.	H_2O.
7·6	1·32	191	44·7	8·42	9·40	7·86	24·8
		154	37·6	7·67	9·51	6·60	19·5
		149	35·8	7·77	9·76	7·11	22·4
		118	30·1	7·90	8·75	7·82	21·4
		101	24·0	10·59	10·85	6·50	21·6
33·0	0·82	222	132·7	5·16	41·9	18·2	—
		195	130·4	5·23	45·0	18·0	24·8
		192	127·8	5·11	44·4	18·2	24·9
		159	118·8	5·25	43·9	20·4	—
		126	113·2	4·94	43·6	21·2	22·3
		126	112·1	5·02	43·9	21·0	25·7
		74·5	76·6	4·85	41·8	21·4	20·9

Some experiments summarised in Table VII show what changes take place in a fog when bubbled through a second wash-bottle; in the examples given, the solution was 1·24*N*-sodium hydroxide in 50% (by vol.) alcohol. The symbols I and II refer to the first and

TABLE VII.

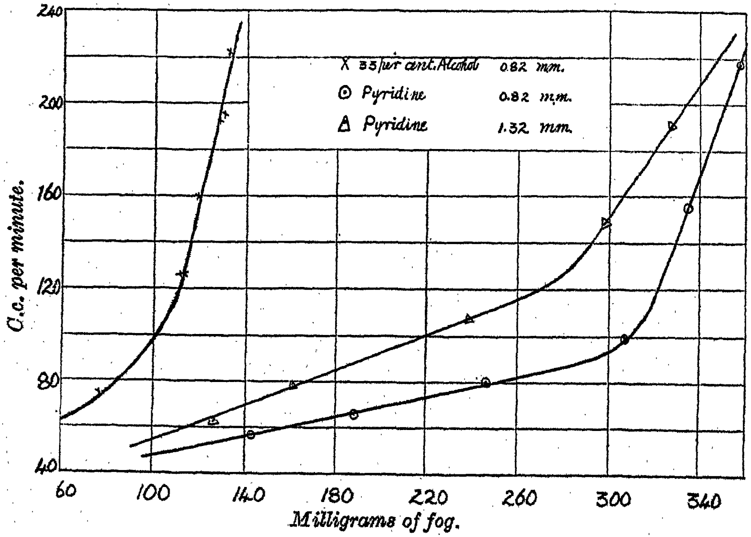
Radius of jet (mm.).		Rate (c.c./min.).	Fog (mg.).		Absorption, %.	HCl in fog, %.	
I.	II.		I.	II.		I.	II.
0·60	0·99	200	172	89·2	48·6	5·2	2·00
0·60	0·99	219	187	105·1	43·9	5·2	2·00
1·66	0·60	200	145	40·8	71·8	4·5	1·60

second wash-bottles, respectively. These figures clearly show how much more effective the narrower jets are for causing absorption of the particles. A great decrease in acid concentration is shown also, which can only be explained by condensation of vapour on the particles; whether this condensation is preferential or not has yet to be determined.

The alcoholic solutions follow the logarithmic law put forward in connexion with the other solutions.

Pyridine Solutions.—Pyridine was used to see whether an organic base would give fogs under the experimental conditions. (Aniline behaves in a similar manner to pyridine.) With an $M/2$-solution, very dense fogs were obtained in which the concentration of acid varied somewhat more than usual with the rate of passage of the gas, decreasing with decrease in the rate. The critical rate of about 110 c.c./min. is shown very distinctly in Fig. 5. During progressive neutralisation of the base, the concentration of acid in the particles remained steady, as also did the partial pressure of aqueous vapour. In this case also, as with the stronger alcoholic solution, the narrower jet was the more effective fog producer.

FIG. 5.



The pyridine solution follows the same law as do the simple aqueous solutions during the process of neutralisation.

The use of pyridine is complicated by its volatility, and this no doubt is one reason that fog was formed in the bubbles as they passed through the solution. This aspect of the question has been examined qualitatively, using solutions of ammonia and of hydrogen chloride of varying concentrations. If air carrying hydrogen chloride is passed through ammonia solutions, fogs are formed in all cases because even in dilute solutions ammonia has an appreciable vapour pressure. If, however, the vapour from even concentrated ammonia is passed through hydrochloric acid solutions, no fog is obtained until an acid solution is used of such high concentration that the partial pressure of the chloride rises above its infinitesimally small values in the dilute solutions. The formation of fogs begins in about 18% acid, and their density increases rapidly as the concentration of the acid rises above this.

Sizes of, and Charges on, the Particles.—Since the partial pressure of the water vapour and the concentration of acid in the fog particles remain practically constant, it would be expected, assuming the system to be in equilibrium, that the particles would all have the same radius, but this expectation is not completely fulfilled.

The apparatus used for studying the size of the fog particles consisted of an inner cylinder of thin, hard glass, surrounded by a thick one, the space between being sealed at each end. Wide-bore taps were used to minimise contact of the fog with surfaces. Light entered on one side by a narrow slit; on another slit at the front the level of the fog surface was read at intervals. The surface of the fog remained level during an experiment except when the densest fogs were being used.

The Stokes–Cunningham equation was used for calculating the radius of the particle from its rate of fall. The equation may be reduced to the form $r = x\sqrt{v}$, where r is the radius in cm., v is the velocity of fall in cm./sec., and x varies according to the viscosity of the medium and the density of the particle. For the aqueous, alcoholic (7·6 and 33·0%), and pyridine solutions with hydrogen chloride, and for the aqueous solutions with hydrogen bromide, x has been given the values 8·92, 9·00, 9·23, 8·92, and $8{\cdot}40 \times 10^{-4}$, respectively, the corresponding densities of the particles having been taken as 1·04, 1·02, 0·97, 1·04, and 1·17.

Experiment showed that the particles had the same radius at all stages of the neutralisation of the solution, but they increased somewhat rapidly in size during the time of settling, this being particularly noticeable in the case of those from the alcoholic solutions. With dense fogs, the particles appear to be smaller than in the other cases. Table VIII gives the radii of a number of dense fogs, 0·62*N*-sodium hydroxide being used (except with pyridine).

In general, the particles became larger as the concentration of

TABLE VIII.

Depth of liquid: 7·5 cm. Radius of jet: 1·32 mm.

Substance.	Conc.	Rate (c.c./min.).	Temp.	Radius (cm.) $\times 10^4$.
Methylene-blue ...	0·02%	210	25·3°	1·62
„ „ ...	0·004%	210	24·7	1·41
Gelatin	0·122% (with 0·5N-NaCl)	210	22·5	1·08
Buxton clay	0·186%	210	25·3	1·19
Pyridine	$M/2$	208	25·5	0·50—1·16
„	„	77	23·8	—1·19

colloid, etc., decreased, as the radius of the jet decreased (rate constant), and as the rate decreased (radius of jet constant). With the alcoholic solutions, the particles given by the stronger solution were somewhat smaller than those given by the weaker. In all cases the particles in the hydrobromic acid fogs were smaller than those obtained under similar conditions with hydrochloric acid.

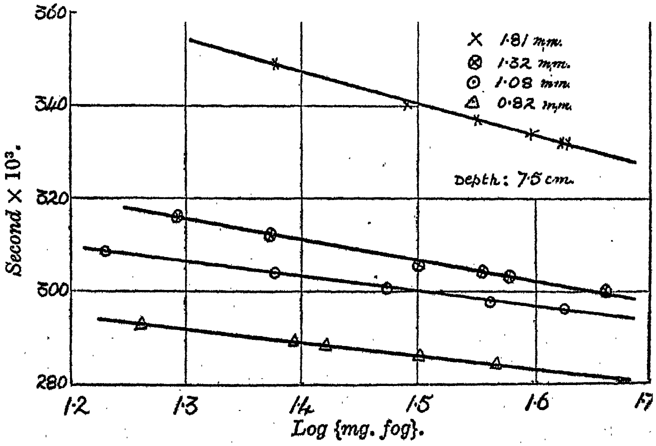
From the various data obtained, it appeared that the original size of the particles is possibly of the same order as for fogs from other reactions, *viz.*, 5×10^{-5} cm.,—pyridine has given particles originally of radius $5{\cdot}0$—$7{\cdot}2 \times 10^{-5}$ cm., methylene-blue of 7×10^{-5} cm. These, however, are very unstable, often increasing rapidly to a mean radius of 2×10^{-4} cm. Whether the comparatively large particles (2—3×10^{-4} cm.) of the fogs from the simple aqueous solutions have grown from smaller particles, it is not possible to say. Apparently an equilibrium state is reached by the particles, since the partial pressure of the water vapour and the concentration of acid remain nearly constant and independent of the conditions of formation. It is hoped to investigate this matter further.

An attempt was made to determine the charges on the particles, but no definite evidence was obtained as to the presence of such charges. This is not surprising in view of the work of Bloch (*Ann. Chim.*, 1911, **22**, 370, 441; **23**, 28), who found that many organic liquids decreased or completely inhibited the formation of charges in a gas bubbling through aqueous solutions in which they were dissolved or on which they formed a layer.

Discussion.

For the rate of absorption of hydrogen chloride (or bromide) from bubbles containing the acid vapour we have $dw/dt = AKP_g$, in which A is the area of the bubble, P_g the partial pressure of the gas, and K the over-all diffusion constant (Lewis and Whitman, *Ind. Eng. Chem.*, 1924, **16**, 1215). Now $dw = -X \, . \, dP$, where X is a function of the molecular weight of the gas; hence, $dP/dt = -AKP_g/X$, or $\log_e P_0/P_t = AKt/X$, where P_0 and P_t are the pressures at times 0 and t. Since in these experiments P_0 and the concentration of acid in the particles are constant, the equation becomes $K'' - K't = \log_e F$, where K'' and K' are constants, and F is the number of mg. of fog per litre of air. This requires that the relation between the time of contact of the bubbles with the solution and the logarithm of the weight of fog should be linear. Fig. 6 shows that this requirement is fulfilled. At the depth of 7·5 cm., as shown in Fig. 6, the lines get slightly steeper as the radius of the jet increases, but it has been found that the similar lines drawn for the depths 3·7 cm. and 5·5 cm. are practically parallel. Moreover, there is not a great difference between the slopes of the lines whatever the size of jet or depth of liquid.

FIG. 6.



On plotting the data obtained in the experiments where the concentration of capillary-active substance was varied, it is found that straight lines are obtained (Fig. 7) corresponding to the general equation $\log_{10} F = m \log_{10} C + K_1$, in which F is the weight of fog (in mg.) formed in the first litre of air used, C is the concentration % of added material, and m and K_1 are constants. The values thus found for m and K_1 for various solutions are given in Table IX, and some typical experimental and calculated values in Table X. It will be seen that the above expression satisfactorily represents the experimental results except for a few very dilute solutions.

The activities of the substances used extend over a wide range; the only generalisation which emerges is that basic substances (*e.g.*, safranine and methylene-blue) are more active than others (*e.g.*, gum arabic and Congo-red). The constant K_1 may be defined as the logarithm of the amount of fog which would be obtained

TABLE IX.

Substance.	Conc. of alkali (N).	m.	K_1.
*iso*Amyl alcohol	0·59	0·274	1·938
Gelatin	0·61	0·284	2·532
Gelatin	1·24	0·287	2·522
Gelatin +0·5N-NaCl	0·61	0·240	2·504
Methylene-blue	0·61	0·218	2·700

Substance.	Conc. of alkali (N).	m.	K_1.
Safranine	0·61	0·446	2·852
Congo-red	0·61	0·385	2·237
Orange G.	0·61	0·370	2·326
Kaolin (1)	0·61	0·508	2·080
Kaolin (2)	0·61	0·385	2·169
Aquadag (1)	0·61	0·286	2·352
Aquadag (2)	0·61	0·390	2·667
Buxton clay	0·61	0·212	2·510

Kaolin and Aquadag (1): partial pressure of HCl, 36·7 mm.
„ „ „ (2): „ „ „ 139·2 „

TABLE X.

Solution: 0·61N-NaOH.

Substance.	%.	Fog (mg.). Found.	Calc.	Remarks.
Gelatin.	0·098	171·8	176	Points are scattered on both sides of the line drawn.
	0·073	156·2	162	
	0·052	142·4	147	
	0·049	143·2	145	
	0·024	123·8	118	
	0·008	87·1	87	
	0·0035	70·5	68	
	0·0016	52·9	54·5	
	0·000	23·4	—	
Methylene-blue.	0·0267	222·8	227	The last two points fall below the values required by the straight line.
	0·0133	195·0	195	
	0·0067	168·1	168	
	0·0027	146·7	138	
	0·0013	117·5	117	
	0·00067	98·1	102	
	0·00027	66·0	83	
	0·0000	31·9	—	
Aquadag (1).	0·194	142·0	141	All the points lie close to the line drawn through them.
	0·130	124·5	126	
	0·065	103·5	103	
	0·039	88·7	89	
	0·026	80·6	79	
	0·013	61·7	65	
	0·000	17·1	—	

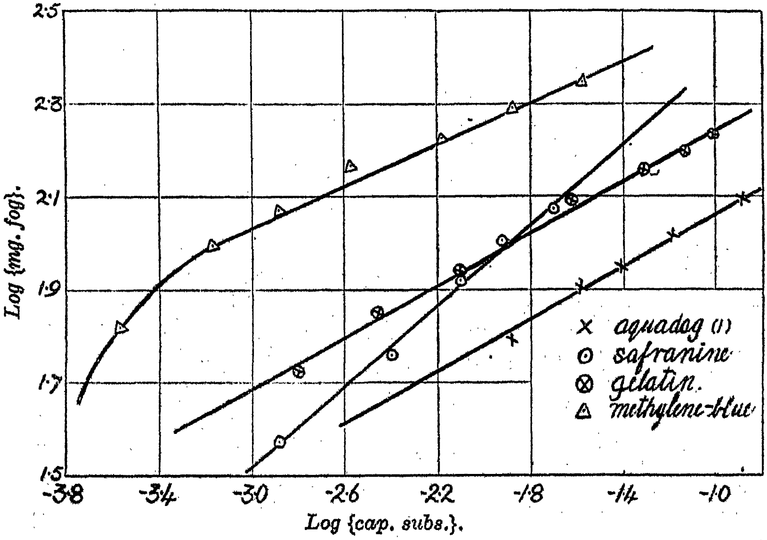
from a 1% solution, provided that the straight-line law held up to that point; K_1 is thus a measure of the activity of the given material. Fig. 7 shows that the slope of each line is a specific property of the corresponding substance, *i.e.*, that the rate of change of fog formation with change in concentration varies from one material to another.

The great capillary activity of such substances as gelatin and methylene-blue has been noticed in other directions (Donnan, *Rep. Brit. Assoc.*, 1923, Sect. B, 12), *e.g.*, *E.M.F.* (Šendera, *Rec. trav. chim.*, 1925, **44**, 480), cataphoresis (van der Grinten, *J. Chim.*

physique, 1926, **23**, 209), water-fall experiments (McTaggart, *Phil. Mag.*, 1914, **27**, 297). As the relation between the amount of material present and the effect it produces is of the same form as the "adsorption isotherm," it has generally been concluded that adsorption at the interface is the cause of the phenomena. The equation given above has the same form as the adsorption isotherm.

It is rather remarkable, however, that such great effects should be obtained, since the surface tensions of these solutions differ very little from that of pure water or of the alkali solutions used. That surface tension is probably not the controlling factor, at any rate so far as fog formation is concerned, is shown by the fact that although amyl alcohol causes great reductions in surface tension it is not very active as regards fog formation.

FIG. 7.



A survey of the possible causes of the decreased rate of absorption of the acid vapours brings out the fact that the seat of the phenomenon lies in the film round the bubble, and that this film is greatly altered by colloids, etc. Moreover, the peculiar properties of this film only appear in alkaline solution. A case of inhibited diffusion of a gas through an alkaline film has been noted by Taylor (*Fuel*, 1926, 5, 195); in this case, the whole system was wet, so that it is not possible to say whether this film behaved towards water vapour in the same way as the alkaline films round the gas bubbles behaved in the present experiments.

A serious problem is that of explaining how all the moisture gets into the bubbles in order to form the great quantities of fog obtained in some cases. It may be that the film acts as a membrane which is readily permeable to water vapour but not so permeable to the acid gas.

In some of the experimental data it is noteworthy that the vapour pressures recorded are greater than correspond to saturation for air at the temperatures given. This is probably connected with the uncertainty attaching to the temperature, for it is difficult to control the heat effects arising from (i) the neutralisation process in the solution, and (ii) the condensation of water to form the fog particles. This uncertainty causes a complication in the attempt to correlate the size of the particles with their acid content. Rothmund (*Monatsh.*, 1918, **39**, 571) used an approximate form of the equation connecting vapour pressure with the radius of curvature of the particle by equating the increase in vapour pressure, due to the increased curvature, to the decrease brought about by dissolved material. The equation obtained finally was $r = 6{\cdot}1 \times 10^{-6}/ci$, where r is the radius of the drop, c the concentration of dissolved material, and i the van 't Hoff factor. With Rothmund's ozone fogs, the formula gives results of the right order, but if it is applied to the results of the present author and of others, the calculated values for the radii are very wide of those actually found. It is a remarkable fact that fog and cloud particles (whether liquid or solid), when formed by spontaneous condensation of vapour, all tend to have a radius of about 5×10^{-5} cm. None of the equations which have been put forward (such as Rothmund's given above, von Weimarn's equation of state, or the equation connecting vapour pressure and radius of curvature) gives any indication of such a "critical" radius. Donnan (*Z. physikal. Chem.*, 1903, **46**, 197) has deduced thermodynamically, however, that a critical radius of about 1×10^{-5} cm. should exist, and Lewis ("System of Physical Chemistry," 1920, I, 332) shows that with oil emulsions there is a distinct tendency for the particles to approximate to this size; but that the same radius should be found general for aerial colloids is certainly remarkable. The comparatively large particles found in the present experiments are probably the result of condensation of vapour on particles originally of this critical radius.

Many of the data recorded in the present investigation suggest that the fog droplets persist even in an unsaturated atmosphere. This is not unexpected, as it is well known that mists formed in the presence of ions can exist for long periods in highly unsaturated atmospheres. But in the present case the uncertainty as to temperatures precludes any definite conclusions on this matter. Further and more accurate information on this and other factors is required before the conditions of stability of these fogs can be completely understood.

Summary.

1. It has been shown that hydrogen chloride and hydrogen bromide vapours are incompletely absorbed by alkaline solutions, more particularly in presence of colloids and dyes. A limiting concentration of hydroxyl ions probably exists below which absorption is complete.

2. The relations between the amount of fog formed and alkali concentration, and also between the amount of fog and the concentration of capillary-active substance, are logarithmic and of the same form as the " adsorption isotherm."

3. The concentration of acid in the fog particles and the partial pressure of the water vapour in contact with them are practically constant.

4. The radii of the particles are smaller the denser the fog produced.

5. No electrical charges have been definitely detected.

The author's best thanks are due to Prof. J. C. Philip for his constant advice during the progress of this work, and to the Governors of the Imperial College of Science and Technology and the New Zealand Government for a Dominion Research Scholarship.

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LONDON, S.W. 7. [*Received, January 15th*, 1927.]

CXXXVII.—*The Purification of Acetic Acid. The Estimation of Acetic Anhydride in Acetic Acid.*

By KENNEDY JOSEPH PREVITÉ ORTON and ALAN EDWIN BRADFIELD.

THOUGH the purity of commercial acetic acids has undergone considerable improvement within the last three or four years, it is still found to be necessary to distil from 2% of chromic oxide, as described by Orton and Bradfield (J., 1924, **125**, 960), in order to obtain an acid free from reactive impurities suitable for a medium for the delicate halogenation experiments which are in progress in this laboratory. The resulting stable acetic acid melts, however, some 0·5° lower than the original acid, owing to the formation of water by oxidation of the impurities, and to obtain an acid melting above 16°, the rather tedious and wasteful process of fractionation was resorted to. It is now found that when acetic anhydride equivalent to the water present is added together with the chromic acid, by simple distillation some 85% of a commercial acid melting at, say, 14·5—15·5° can be converted into a stable acid melting at 16·2—16·4°.

It was shown by Orton and M. Jones (J., 1912, **101**, 1708) that, unless a catalyst be present, the hydrolysis of acetic anhydride in glacial acetic acid is a slow process, but that strong acids have a powerful catalytic effect. The chromic acid used in the above process acts as the necessary catalyst so effectively that the distillate contains not more than 5 parts of acetic anhydride per 100,000, an amount which is generally negligible, and gradually falls to zero on keeping.

The following illustrates the method. A commercial acetic acid melted at 14·2°. If distilled from chromic oxide alone, a main fraction melting 0·5° lower, *i.e.*, at 13·7°, would be obtained. If the melting point of the anhydrous acid be taken as 16·6°, and the lowering of the melting point as 0·2° for each 0·1% of water present (de Visser, *Rec. trav. chim.*, 1893, **12**, 101), this would correspond to 1·45 g. of water per 100 g. of acid. To each 100 g. of acid were therefore added $1{\cdot}45 \times 102/18 = 8{\cdot}22$ g. of acetic anhydride, and 2 g. of chromic oxide. The mixture was heated to just below the boiling point for ½ hour, and then distilled, a short still-head being used to prevent traces of chromic acid being carried over as spray. A first fraction of 10—15% was neglected; the remainder, collected as one fraction, melted at 16·2°, had a bromine absorption number of 1·1 (Orton and Bradfield, *loc. cit.*), and, tested as described below, was found to contain 0·0047 g. per cent. of acetic anhydride. An acid purified in this manner which had been standing for 3 months contained no trace of acetic anhydride. It should be noted that if halogen is present in the original acetic acid, chromium will appear in the distillate.

For the rectification of an acid previously distilled from chromic acid alone, distillation in a similar way of a mixture with the theoretical amount of acetic anhydride (no further lowering of melting point of 0·5° being allowed for in this case) together with 0·2 g. per cent. of β-naphthalenesulphonic acid as a catalyst, is equally effective.

A further examination of the effect of possible impurities on the "absorption" of chlorine and bromine by acetic acid indicates that the high "absorption number" for bromine shown by commercial acids is probably due mainly to formic acid, whilst the presence of 0·15 g. per cent. of acetone causes an appreciable absorption of chlorine. The presence of a manganese salt or of ethyl alcohol has little effect.

The Estimation of Acetic Anhydride in Acetic Acid.—In 1911, Orton and Edwards (J., 99, 1181) developed a method of estimation of acetic anhydride in acetic acid based on the knowledge that 2 : 4-dichloroaniline is rapidly and completely acetylated by acetic anhydride, whilst, at the ordinary temperature, acetic acid is without action. The method has been modified by Spencer (*J. Assoc. Offic. Agric. Chem.*, 1923, **6**, 493), who used ordinary aniline in place of the 2 : 4-dichloroaniline, and after separation of the aniline and anilide by a method similar to that employed by Orton and Edwards, titrated the anilide, after hydrolysis, with a bromate–bromide solution; and by Calcott, English, and Wilbur (*Ind. Eng. Chem.*, 1925, **17**, 942), who used the dichloroaniline, and titrated the excess with nitrous acid.

In the present modification, 2 : 4-dichloroaniline is added to the acetic acid, containing anhydride, and the excess aniline estimated by titration with bromate–bromide solution, without separation from the anilide formed. To 75 c.c. of the acid to be tested, 10 c.c. of a solution of 2 : 4-dichloroaniline in acetic acid (containing approximately 3 g. in 250 c.c.) were added. Next morning, the solution was diluted with 85 c.c. of water, 10 c.c. of 10% hydrochloric acid were added, and then 10 c.c. of 1·862*N*/10-bromate–bromide solution. The flask was corked, and potassium iodide added after 5 minutes. 9·60 C.c. of 1·005*N*/20-thiosulphate were required. In a control, in which 75 c.c. of an acid known to contain no anhydride were used, and the other quantities and the procedure were the same, the titre was 8·43 c.c. of 1·005*N*/20-thiosulphate. Hence the aniline acetylated is equivalent to (9·60 − 8·43) × 1·005 c.c. of *N*/20-bromine, and the acetic anhydride = 0·004 g. per 100 c.c. (Br_2 equivalent $C_6H_3Cl_2{\cdot}NH_2$).

The method was tested by the titration of the aniline in the presence and the absence of 2 : 4-dichloroacetanilide, and more rigorously by the addition of known quantities of acetic anhydride to acetic acid, and actual estimation thereof. The following results were obtained :

Anhydride (g.) added to 75 c.c. of acid.	Anhydride found. (a).	(b).
0·0955	0·0936	—
0·0478	0·0479	0·0470
0·00955	0·00951	0·00942

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[*Received, March 17th,* 1927.]

CXXXVIII.—*The Chlorination of Anilides. The Directing Influence of the Acylamido-group.*

By KENNEDY JOSEPH PREVITÉ ORTON and ALAN EDWIN BRADFIELD.

Proportions of the Isomerides formed by Chlorination.

IN 1909, Orton and W. Jones (J., 1909, 95, 1056) showed that the chlorination of acetanilide, in acetic acid solution, by the addition of the calculated quantity of bleaching powder solution yielded some 40% of *o*-chloroacetanilide, the remainder of the acetanilide being converted into the *p*-isomeride. This investigation was extended to other acylanilides by Orton and King (J., 1911, 99, 1377). These authors aimed at an actual separation of the products of chlorination by a process of crystallisation of the anilides and fractional steam distillation of the anilines obtained by hydrolysis, and estimated the proportions of the isomerides formed from the yields of pure substances obtained. In addition, Orton and King (J., 1911, 99, 1369) measured the velocity coefficients for the reaction between various anilides and chlorine.

On reviewing these results subsequently, it was felt that some uncertainty would attach to any deduction, bearing on the problem of the directing influence of the acylamido-group on nuclear substitution, made by a correlation of these two series of measurements, since the estimate of the proportions of the isomerides formed was not so satisfactory as could be desired, for the reasons stated below. First, the method of chlorination involves the gradual dilution of the acetic acid medium by the bleaching powder solution used for chlorination, so that in the experiments referred to the medium varied from 100% to 50% acetic acid as the chlorination progressed. The results obtained by Holleman, Hartogs, and van der Linden (*Ber.*, 1911, 44, 704) showing the marked effect of medium on the nitration of anilides suggest that the values obtained for the proportions of *o*- and *p*-chloro-compounds may actually represent a kind of average for more or less dilute acetic acid medium. Secondly, the actual isolation of the isomerides in a pure state involves a number of processes, which from their nature cannot be carried out in an exactly quantitative way. A re-determination was therefore undertaken.

In the present series of experiments, the composition of the chlorination product of acetanilide was determined by the freezing-point method, without any attempt at preliminary separation, and confirmed by a quantitative separation by sublimation of the *o*- and *p*-chloroacetanilides, a process which is very readily carried out.

In experiments on other acylanilides, these were first hydrolysed, and the anilines acetylated for analysis.

The delicate method of chlorination introduced by Orton and King (J., 1911, 99, 1185), based on the reversible reaction between a chloroamine and hydrochloric acid,

$$>NCl + HCl \rightleftharpoons Cl_2 + >NH,$$

lends itself admirably to the present purpose. With many chloroamines, in glacial acetic acid, the equilibrium lies almost entirely to the right, and since the equilibrium is attained almost instantaneously, the addition of hydrochloric acid to a solution of a chloroamine results in the liberation of an exactly measured quantity of chlorine at the moment required. Moreover, since nucleus chlorination results in the liberation of hydrochloric acid equivalent to the chlorine used, the addition of a trace of hydrochloric acid suffices for complete chlorination, thus avoiding a high concentration of chlorine at any period of the reaction and the formation of anilide hydrochlorides in anhydrous solutions.

For the chlorination of acetanilide, the chloroamine most suitable as a source of chlorine is that of acetanilide itself, *i.e.*, the reaction is most readily carried out by allowing *N*-chloroacetanilide to undergo the so-called " transformation " (Orton, *Brit. Assoc. Reps.*, 1910, 85):

$$C_6H_5{\cdot}NClAc \longrightarrow C_6H_4Cl{\cdot}NHAc\ (o- + p-).$$

The possibility presents itself that at the moment of liberation of chlorine from *N*-chloroacetanilide, the acetanilide molecule may be in a special "reactive" state, and that the proportions of the isomerides formed may differ from those formed when the chlorine is not generated in this way. This, however, is not the case, as is seen from Table I, where the mean values from several experiments for the percentage of *p*-chloroacetanilide formed by the "transformation" of *N*-chloroacetanilide and by the chlorination of acetanilide by chlorine derived from another chloroamine are given for different media. The remainder of the product is the ortho-compound in each case.

TABLE I.

Chlorination at 20°.

Medium.	Percentage of para. Chlorination of acetanilide.	Transformation of *N*-chloroacetanilide.
Chloroform	68·8	69·8
Acetic acid	67·5	66·8
50% Acetic acid	60·7	57·3
Methyl alcohol	60·6	—

It is seen from the above table that the medium has only a small effect on the proportions of *o*- and *p*-isomerides. No explanation is at present offered to account for the differences between the values for 50% acetic acid, which seem to be rather greater than the experimental error involved.

In Table II is shown the percentage of the isomerides formed by the chlorination of several anilides. The most striking feature of these results is that although the acids corresponding to the acyl groups differ so largely in strength as measured by their ionisation constants, in molecular weight, and in "space-filling power," yet the proportions of the isomerides are practically the same in each case.

TABLE II.

Chlorination in acetic acid, m. p. 16°, at 20°.

Anilide.	% ortho.	% para.
Formanilide	30·1	69·9
Acetanilide	32·5	67·5
Benzanilide	30·4	69·6
Benzenesulphonanilide	35·0	65·0

Similarly, the nitration of formanilide, acetanilide, and benzanilide under the same conditions yields approximately the same proportions of *o*- and *p*-nitroanilides (Holleman, Hartogs, and van der Linden, *loc. cit.*).

Velocity of Chlorination of Anilides.

Orton and King (*loc. cit.*) found it possible to employ their method of chlorination for the measurement of the velocity of the reaction between chlorine and anilides in acetic acid solution, a reaction which is found to be of the simple bimolecular type. Their measurements are for an acetic acid containing 0·14% of water, as a medium, at a temperature of 16°. The velocity of chlorination is found to be very sensitive to the medium effect of water, increasing rapidly as the proportion of water is increased.

The experiments described above on the proportions of the isomerides formed were carried out at 20°, in an acetic acid, m. p. 16°, *i.e.*, containing about 0·3% of water. The velocity determinations have been repeated at 20°, in a medium containing 1% of water, the errors due to slight variation in the water content being thereby minimised. Column 1 of Table III gives the velocity coefficients at 20° for perfectly standard conditions, namely, anilide and chlorine both initially at 0·0025 mol./litre; hydrochloric acid 0·0125 mol./litre; medium, acetic acid with 1% of water. In column 2 are Orton and King's values for these and other anilides, and in column 3 the ionisation constants of the acids $R{\cdot}CO_2H$, corresponding to the groups $R{\cdot}CO{\cdot}NH-$, are given for reference.

TABLE III.

Velocity coefficients.

Anilide.	O. and B. (H_2O = 1%).	O. and K. (H_2O = 0·14%).	Ionisation constant of $R{\cdot}CO_2H$. $K \times 10^5$.
Formanilide	9·2	4·95	21·4
Acetanilide	62·2	40·0	1·86
Propionanilide	—	72·0	1·34
Butyranilide	—	64·5	1·49—1·75
*iso*Valeranilide	—	57·0	1·67—1·73
Benzanilide	69·1	42·0	6·8
Benzenesulphonanilide	42·7	—	—

The amount of hydrochloric acid employed produces an appreciable effect on the velocity of chlorination, the effect on acetanilide being a decrease in speed as the hydrochloric acid is increased, although with formanilide and benzenesulphonanilide this effect is reversed (see Table IV). The validity of the correlation of the velocity measurements under standard conditions with the measurements of the proportions of the isomerides formed remains unimpaired by the slight differences in medium in the two sets of experiments, since the latter values are but little affected by large variations in the medium.

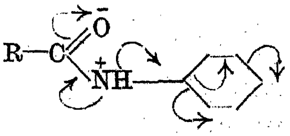
TABLE IV.

Chlorination in 99% acetic acid at 20°.

Molar proportions of HCl added :—	1·5	5	10	20
k for :				
Formanilide	8·9	9·2	—	10·2
Acetanilide	66·5	62·2	59·6	55·7
Benzanilide	—	69·1	—	—
Benzenesulphonanilide	41·5	42·7	44·4	46·9

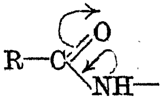
Discussion of Results.

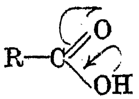
The bearing of modern theories on the rates of entrance of chlorine into a given position, either ortho or para, for the different anilides may be briefly examined. According to Allan, Oxford, R. Robinson, and Smith (J., 1926, 403) and Ingold and Ingold (*ibid.*, p. 1311), the directing influence of the acylamido-group is to be attributed to the tendency of the nitrogen atom to act as an electron source, as modified by a betaine-like electronic conjugation with the oxygen of the carbonyl group :



Both these processes result in the acquirement of a positive charge by the nitrogen atom. The tendency for the nitrogen to act as an electron source towards the nucleus is said to be the greater the more negative (or less positive) it is originally.

The process I (below) is exactly analogous to the process leading to the ionisation of the corresponding carboxylic acid (Allan, Oxford, Robinson, and Smith, *loc. cit.*, p. 405; Lea and Robinson, *ibid.*, p. 2352), so that whatever effect R may have on (II) should also be manifest to a greater or lesser extent in (I), that is, the greater the

(I.) 

 (II.)

strength of the acid (II) the greater the tendency of the nitrogen in (I) to acquire a positive charge by this process, and hence the lesser tendency of the nitrogen atom to act as an electron source toward the nucleus. Hence the directing effect of the group R·CO·NH· should decrease with increase in the ionisation constant of the acid $R{\cdot}CO_2H$.

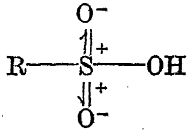
According to Allan, Oxford, Robinson, and Smith (*loc. cit.*, p. 407), in comparing the directive powers of groups it may be considered that what is being compared is the number of occasions in unit time that effectual polarisations take place, *i.e.*, the velocity of substitution at a given carbon atom is the measure of the directive power of a group. In the present case, since the different acyl groups do not alter the proportions of the isomerides appreciably, the velocity coefficients given in Table III, column 1, may be taken directly as a comparative measure of the directing effects of the groups concerned on either the ortho- or the para-position. These are seen to be in the order $C_6H_5{\cdot}CO{\cdot}NH^- > CH_3{\cdot}CO{\cdot}NH^- > H{\cdot}CO{\cdot}NH^-$, whereas from the foregoing theoretical considerations the order should be $CH_3{\cdot}CO{\cdot}NH^- > C_6H_5{\cdot}CO{\cdot}NH^- > H{\cdot}CO{\cdot}NH^-$.

If it be assumed, as would appear to be reasonable, that the proportions of the isomerides formed by the chlorination of propionanilide, butyranilide, and *iso*valeranilide are not very different from those formed by the chlorination of acetanilide, the velocity coefficients obtained by Orton and King lead to the series :

$$C_2H_5{\cdot}CO{\cdot}NH^- > \begin{matrix} C_3H_7{\cdot}CO{\cdot}NH^- \\ C_4H_9{\cdot}CO{\cdot}NH^- \end{matrix} > C_6H_5{\cdot}CO{\cdot}NH^- >$$
$$CH_3{\cdot}CO{\cdot}NH^- > H{\cdot}CO{\cdot}NH^-$$

corresponding with the theoretical sequence, except that again the group $C_6H_5{\cdot}CO{\cdot}NH^-$ should follow $CH_3{\cdot}CO{\cdot}NH^-$, instead of preceding it.

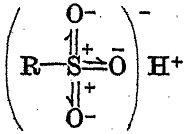
The benzenesulphonamido-group requires special consideration, since here no betaine-like process of electronic conjugation takes place. The ionisation of a sulphonic acid may be attributed to the effect of the positive charges on the sulphur atom, which tend to loosen the binding between the hydroxyl oxygen and the hydrogen atom,



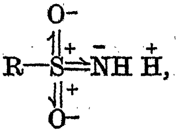
$$R-\overset{\overset{\displaystyle O^-}{\uparrow\|+}}{\underset{\underset{\displaystyle O^-}{\downarrow\|+}}{S}}-OH$$

In a similar way, the nitrogen atom of a sulphonanilide is rendered somewhat positive, and although perhaps it is not justifiable to compare the effect of the sulphonyl group with that of a carboxyl group, since a different mechanism is called into play, from the consideration of the strength of a sulphonic acid, it is rather surprising to find the benzenesulphonamido-group nearly as strongly directing as the acetamido-group.

On an alternative view, the ionisation of a sulphonic acid may be attributed to the tendency of a sulphur atom to act as the positive end of a semipolar bond, a tendency which is satisfied in its higher valency states. Hence we have in a sulphonic acid, and in a sulphonamide, the tendency towards the following :



$$\left(R-\overset{\overset{\displaystyle O^-}{\uparrow\|+}}{\underset{\underset{\displaystyle O^-}{\downarrow\|+}}{S}}\rightleftharpoons\overset{-}{O}\right)^- H^+$$



$$R-\overset{\overset{\displaystyle O^-}{\uparrow\|+}}{\underset{\underset{\displaystyle O^-}{\downarrow\|+}}{S}}\rightleftharpoons\overset{-}{N}H\ \overset{+}{H},$$

a tendency which, with the sulphonamide, is fulfilled when salt formation takes place (compare Clarke, Kenyon, and Phillips, J., 1927, 188). In the sulphonanilide, then, the nitrogen atom is tending to become negative, but forming a dipole arrangement (Goss, Ingold, and Wilson, J., 1926, 2440; Baker and Ingold, *ibid.*, p. 2462) with the proton. Although it is difficult to foresee the extent to which this dipole arrangement affects the tendency of the group to act as an electron source towards the nucleus, nevertheless this view appears more in harmony with the fact that the rate of chlorination of benzenesulphonanilide is more rapid than that of formanilide.

An extension of this investigation to other compounds containing the groups –NRR and –OR is in progress.

EXPERIMENTAL.

Analysis of Mixtures of o- *and* p-*Chloroacetanilides.—Melting-point method.* The melting point of the chlorination product of acetanilide was determined by the method described by G. Owen (J., 1923, **123**, 3394) and the composition read off from a curve constructed from the data given by Orton and G. Owen (J., 1924, **125**, 766) for the melting points of mixtures of *o*- and *p*-chloroacetanilides. In some of the earlier experiments the eutectic point was determined, after the addition of a known quantity of the ortho-compound to bring the composition of the mixture to the region where the eutectic point could be realised, to demonstrate the absence of a third substance. The method, however, lacks accuracy, and was not employed after the development of the sublimation method of obtaining an independent check on the composition of the chlorination product.

Sublimation method. The difference between the vapour pressures of *o*- and *p*-chloroacetanilides (Sidgwick and Rubie, J., 1921, **119**, 1013) would suggest that at least a partial separation of the isomerides could be obtained by sublimation. It is found that the separation is quantitative when the sublimation is carried out in the following way. The finely powdered mixture of *o*- and *p*-chloroacetanilides is spread in a thin layer on a watch glass which is placed on the top of an air-oven, and a wide funnel clamped over it in an inverted position so that the edge of the funnel just clears the watch glass.

The internal temperature of the oven is maintained at 110°, the temperature of the solid on the watch glass probably being about 50—60°. The *o*-chloroacetanilide sublimes and condenses to some extent on the sides of the funnel, although part escapes through the stem (dimensions of funnel employed : width 10 cm., length 17 cm.). The watch glass and contents are weighed from time to time, and after 12—15 hours' heating are at a constant weight. In a control experiment, a mixture containing 62·4% of *p*-chloroacetanilide gave, by this method, (*a*) 62·3%, (*b*) 61·8% of the para-compound. The residual solid melted sharply at 178°, and was therefore completely free from the ortho-compound. The presence in the mixture to be analysed of any *m*-chloroacetanilide, which is non-volatile under these conditions, shows itself by the lowering of the melting point of the solid remaining, whilst unchanged acetanilide or 2 : 4-dichloroacetanilide volatilises so slowly that when 3—4% is present a constant weight is not attained even after 36 hours' heating. In no case did the sublimation method of analysis give any indication of a third substance in the chlorination products here described.

Method of Chlorination.—The selection of a chloroamine for use as a source of chlorine (Orton and King, *loc. cit.*) is in the present case guided by the following considerations : (1) The chloroamine must be stable, and readily obtained in a state of purity, (2) a quantitative separation of the parent substance from the chlorinated product must be possible. Two chloroamines fulfil these requirements, chloroacetamide, the acetamide being readily soluble in water, and *p*-toluenesulphondichloroamide, "dichloramine T," the sulphonamide being readily soluble in alkali, whilst the chloroanilides are almost insoluble in water or alkali.

Dichloramine T was prepared as follows (compare Chattaway, J., 1905, **87**, 145; Kraus and Crede, *J. Amer. Chem. Soc.*, 1917, **39**, 2720). 10 G. of *p*-toluenesulphonamide are dissolved in 100 c.c. of acetic acid, and 120 c.c. of a 2·5*N*-solution of bleaching powder slowly run in with shaking and cooling. The fine crystalline powder is collected, and without drying dissolved in 75 c.c. of hot acetic acid, and reprecipitated by the addition of 37 c.c. of *N*/10-bleaching powder solution. Yield, 15 g. (Found: Cl, by titration, 29·43. Calc.: Cl, 29·53%).

Preparation of Chloroacetamide (compare Hofmann, *Ber.*, 1882, **15**, 407; Hantzsch and Dollfuss, *Ber.*, 1902, **35**, 252; Mauguin, *Ann. Chim. Phys.*, 1911, **22**, 297; Boismenu, *Compt. rend.*, 1911, **153**, 1482).—A good yield is obtained by dissolving 35 g. of acetamide in 80 c.c. of water, and adding 50 g. of sodium bicarbonate. A fairly rapid current of chlorine is led in, the solution being kept cool. After a time, the bulky mass of chloroacetamide and sodium chloride is filtered off, and after the addition of a further quantity of sodium bicarbonate to the filtrate the passage of chlorine is continued. The combined solid products are dried and extracted with warm chloroform, the sodium chloride is filtered off, and on cooling, the chloroacetamide separates. Yield, 34 g. (Found: Cl, by titration, 38·01. Calc.: Cl, 37·97%).

Chlorination of Acetanilide in Chloroform.—The chloroform used was washed with water, kept over lime, and filtered before use. In early experiments, about 10 g. of acetanilide together with the requisite quantity of chloroacetamide were dissolved in chloroform, and about 1/10 molar proportion of hydrochloric acid was added. When chlorination was complete, as indicated by titration, the chloroform was removed by distillation and the residue extracted with a small quantity of water. The solid so obtained melted to a dark-coloured liquid and rapidly became dark-coloured in air, and it would appear that some by-product, presumably an oxidation product, is formed during chlorination. The following process, involving a purification of the crude product, was therefore adopted. 2·7 G. (1 mol.) of acetanilide and 2·4 g. of dichloramine T (0·5 mol.) were dissolved in 50 c.c. of chloroform and placed in a thermostat at 20°, hydrochloric acid (0·09 mol.) being added in the form of a concentrated aqueous solution. After 5 hours, chlorination was complete and the chloroform was removed by distillation. The solid residue in the flask was boiled under reflux with 50 c.c. of 10% sulphuric acid for 2 hours, the whole dissolving to a straw-coloured solution, which was made alkaline and distilled in steam. The anilines passing over were collected with chloroform and acetylated by the addition of acetic anhydride to the chloroform solution, the chloroform being allowed to boil away during the acetylation. The excess acetic anhydride and acetic acid formed were removed in a vacuum desiccator over sodium hydroxide. That this method of purification and isolation effects no noteworthy alteration in the proportion of the isomerides is shown by a control experiment, in which a mixture of *o*- and *p*-chloroacetanilides, m. p. 149·7°, after being put through the complete process melted at 149·2°.

The yield and analytical data for duplicate experiments are appended.

(*a*) Yield 96·8%, m. p. 157·7° = 69·5% para. Eutectic point 76·6°, from curve 77°. Sublimation gave 68·3%, 68·1% para.

(*b*) Yield 93·2%, m. p. 156·4° = 68% para. Eutectic point 77°. Sublimation gave 67·4%, 67·4% para.

Chlorination in Acetic Acid.—The acetic acid used, after purification as described by Orton and Bradfield (J., 1924, **125**, 960), melted at 16°. After chlorination with dichloramine T in a manner exactly similar to that described above, the acetic acid was removed by distillation under 11 mm. pressure. The product was hydrolysed, distilled in steam, etc., as before.

(*a*) Yield 92%, m. p. 156·5° = 68% para. Sublimation gave 67·5%, 67·5% para.

(*b*) Yield 91%, m. p. 156·0° = 67·3% para. Sublimation gave 67·0%, 67·0% para.

Chlorination in 50% *Acetic Acid.*—As dichloramine T is only slightly soluble in 50% acetic acid, the use of a large bulk of liquid is avoided by the following procedure. 2·7 G. of acetanilide (1 mol.) were dissolved in 50 c.c. of 50% acetic acid, to which 0·09 mol. of concentrated hydrochloric acid was added, and placed in a bath at 20°. The calculated quantity of a solution of dichloramine T in glacial acetic acid was run in in small portions, simultaneous addition of water keeping the medium as nearly 50% as possible. The solution was evaporated to dryness under a pressure of 11 mm., and the product worked up as before.

(*a*) Yield 93·8%, m. p. 150·6° = 60·7% para. Sublimation gave 61·3%, 61·2% para.

(*b*) Yield 90·6%, m. p. 150·4° = 60·5% para. Sublimation gave 60·5% para.

Chlorination in Methyl Alcohol.—Methyl alcohol "free from acetone" is only slowly attacked by chlorine. Nevertheless, for the chlorination, which was carried out in the usual way, a 5% excess of dichloramine T was taken to compensate for that lost by reaction with the medium. When chlorination was complete, the methyl alcohol was distilled off under diminished pressure, and the product hydrolysed, etc., as before.

(*a*) Yield 89%, m. p. 150·2° = 60·2% para. Sublimation gave 61·2%, 61·1% para.

(*b*) Yield 91%, m. p. 150·5° = 60·5% para. Sublimation gave 60·5%, 60·6% para.

Transformation of N-*Chloroacetanilide.*—*N*-Chloroacetanilide was prepared by the method described by Chattaway and Orton (J., 1899, **75**, 1046), and the transformation effected in the various solvents by the addition of 1/10 molar proportion of hydrochloric acid, in a manner completely analogous to the chlorination experiments described above. The isolation of the product was also carried out in the same way. Analytical data :

Transformation of N-*chloroacetanilide in chloroform.* (*a*) Yield 90%, m. p. 158·0° = 69·8% para. Sublimation gave 69·9%, 69·6% para.

(*b*) Yield 89%, m. p. 157·8° = 69·6% para. Sublimation gave 70·0%, 70·0% para.

Transformation of N-*chloroacetanilide in acetic acid.* (*a*) Yield 89%, m. p. 155·7° = 67% para. Sublimation gave 67·5%, 67·5% para.

(*b*) Yield 89%, m. p. 155·0° = 66·0% para. Sublimation gave 66·4%, 66·7% para.

Transformation of N-*chloroacetanilide in* 50% *acetic acid.* (*a*) Yield 92·3%, m. p. 146·9° = 56·9% para. Sublimation gave 57·8%, 57·8% para.

(*b*) Yield 92·9%, m. p. 146·6° = 56·6% para. Sublimation gave 57·6%, 57·8% para.

Chlorination of Formanilide in Acetic Acid.—2·42 G. (1 mol.) of formanilide, m. p. 48°, and 2·4 g. (0·5 mol.) of dichloramine T were dissolved in 50 c.c. of acetic acid, maintained at 20°, and hydrochloric acid (0·09 mol.) was added. The acetic acid was removed under diminished pressure. The product was hydrolysed with a mixture of equal volumes of concentrated sulphuric acid and water, and the anilines were distilled in steam, collected as for acetanilide, and acetylated for analysis.

(*a*) Yield 84%, m. p. 157·5° = 69·2% para. Sublimation gave 69·4%, 69·7% para.

(*b*) Yield 85%, m. p. 158·0° = 69·9% para. Sublimation gave 71·0%, 70·9% para.

Chlorination of Benzanilide in Acetic Acid.—Benzanilide, m. p. 162°, requires 200 c.c. of acetic acid to dissolve 3·94 g. Chlorination was effected in the above-described manner, the product hydrolysed with a mixture of 1 volume of concentrated sulphuric acid and 2 volumes of water, and the anilines were distilled in steam and acetylated for analysis.

(*a*) Yield 92%, m. p. 157·9° = 69·7% para. Sublimation gave 68·8%, 68·7% para.

(*b*) Yield 92%, m. p. 158·7° = 70·7% para. Sublimation gave 69·4%, 69·6% para.

Chlorination of Benzenesulphonanilide in Acetic Acid.—The chlorination of benzenesulphonanilide, m. p. 110°, was carried out in the usual way. Sulphuric acid of 60% strength is needed for the hydrolysis of the chloroanilides. The anilines obtained were acetylated for analysis.

(*a*) Yield 86·4%, m. p. 154° = 65% para. Sublimation gave 64·3%, 64·3% para.

(*b*) Yield 90%, m. p. 154·4° = 65·4% para. Sublimation gave 65·5%, 65·4% para.

Velocity Determinations.—The determination of the velocity of chlorination of the anilides was carried out by the method described by Orton and King (*loc. cit.*), who used *N* : 2 : 4-trichloroacetanilide as a source of chlorine. This chloroamine and dichloramine T were both used in the experiments now described, the same values for the coefficients being obtained whichever chloroamine was employed.

The anilide was dissolved in 40—50 c.c. of acetic acid, m. p. 16·2—16·4°, prepared as described by Orton and Bradfield (this vol., p. 983), in a 100 c.c. flask, and the required quantity of a freshly standardised solution of the chloroamine run in. The amount of water which, together with the water present in the acetic acid and that to be added with the hydrochloric acid (of which a constant-boiling solution was used), would make up 1 c.c. was added, and the solution made up with acetic acid nearly to the 100 c.c. mark. When the solution had attained the temperature of the thermostat, 20° ± 0·05°, the necessary amount of hydrochloric acid was added, the contents of the flask rapidly mixed by shaking, and the flask replaced in the thermostat. 10 C.c. were removed at intervals and run into potassium iodide solution, the time of half delivery of the pipette, which could be estimated to ± 2 sec., was noted, and the liberated iodine titrated with *N*/100-thiosulphate, with the usual precautions to secure a good end-point.

The loss of chlorine to the vapour phase, consequent upon increasing the air space in the flask, has an appreciable effect if more than three or four portions are removed in any one experiment, so that in these experiments measurements were limited to a few titres during the middle period of the reaction (35%—65% change). Further, since the object in view is to obtain figures which shall represent the relative speeds of chlorination under standard conditions, rather than to establish the true bimolecular nature of the reaction, measurements were only made with anilide and chlorine at the same initial concentration, which was 0·0025 mol./litre in every case.

The velocity coefficient, k, was calculated from the expression $k = x/at(a - x)$, the time being expressed in minutes. The values given above (Table IV) represent the mean values for at least two concordant experiments. As an example of the constancy of k in any one experiment, the following is quoted as typical:

Chlorination of benzenesulphonanilide.

a = 0·0025 mol./litre. HCl = 0·00375 mol./litre.

Time (±0·03 min.).	% changed.	k.
7·02	39·6	40·8
13·28	57·9	41·4
16·97	63·7	41·3
	Mean	41·2

The reproducibility of the values is shown by the following data for the velocity measurements for acetanilide:

Chlorination of acetanilide.

Molar proportions of HCl.	Mean values of k for individual experiments.	Mean k.
1·5	67·0, 66·0	66·5
5	62·8, 60·9, 62·8	62·2
10	59·5, 60·4, 57·9, 60·0, 60·2	59·6
20	55·6, 55·8	55·7

One of us (A. E. B.) wishes to express his thanks to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant.

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BANGOR.

[*Received, March 17th*, 1927.]

CXXXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XVIII. Mechanism of Exhaustive Methylation and its Relation to Anomalous Hydrolysis.*

By WALTHER HANHART and CHRISTOPHER KELK INGOLD.

THE decomposition of quaternary ammonium compounds has been extensively investigated and often exploited for the synthesis of olefins and the degradation of complex bases; nevertheless, no general theory of the mechanism of the process seems to have been advanced. Unquestionably the facts to be explained are numerous and complex; in particular, a satisfactory theory should embrace the following points:

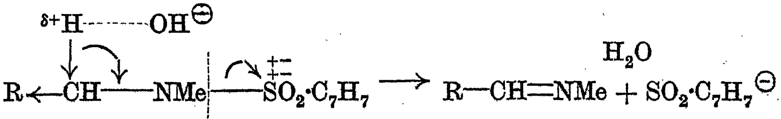
(1) The hydrogen atom eliminated along with hydroxyl in the reaction $R{\cdot}CH_2{\cdot}CH_2{\cdot}NR'_3{\cdot}OH = R{\cdot}CH{:}CH_2 + NR'_3 + H_2O$ is apparently one of those attached to the second carbon atom from the nitrogen atom. Assuming that this is definitely the case (below), then, since one can hardly suppose otherwise than that the cause of molecular instability originates in the ammonium group, it must be explained, first, how the necessary reactivity is propagated to such a distant hydrogen atom through two intervening *saturated* carbon atoms without imparting *en route* a still greater reactivity to the hydrogen atoms attached to the first carbon atom, and, secondly, why the transmitted effect emerges just where it does.

(2) When the four alkyl groups attached to the nitrogen atom are such that different olefins might be produced by decomposition in different directions, the one actually formed has always been found to be ethylene if an ethyl group is present. It is shown below that this generalisation, sometimes referred to as Hofmann's rule, is subject to certain exceptions: the reasons for the rule and the causes of the exceptions both require elucidation.

(3) The synthesis of olefins from quaternary ammonium hydroxides sometimes fails owing to the elimination of an alcohol: $R^1R^2R^3R^4N{\cdot}OH = R^1R^2R^3N + R^4{\cdot}OH$. It is desirable to be able to foretell when and to what extent this is likely to take place.

(4) Quaternary ammonium salts (*e.g.*, chlorides) often decompose differently from the hydroxides. In certain cases both chlorides and hydroxides give corresponding products, but where a difference exists it is the hydroxide which yields the olefin and the salt which gives the alkyl halide or ester. Moreover, the chloride usually decomposes less easily than the corresponding hydroxide. Since both are strong electrolytes and the organic ion is the same in each, these differences of reactivity and their lack of complete uniformity both require explanation.

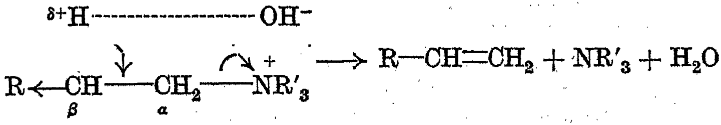
The hypothesis which, we believe, suffices to interpret all these phenomena was outlined in Part IV (J., 1926, 1305) in connexion with hydrolysis, and may be expressed in general terms as follows: Hydrogen atoms in organic molecules, even those in hydrocarbon radicals, exist to a greater or less degree in a condition of incipient ionisation depending on the electron-affinity of the surrounding groups, $\leftarrow C \leftarrow H(\delta +)$; when a hydrogen atom is abstracted as hydrion by a reagent having sufficient proton-affinity to effect its removal in this form, the electrons which held it become absorbed into the residue of the molecule in a manner which again is determined by the electron-affinity of the groups present. The proton-affinity of a reagent is measured by the electrolytic dissociation of its compound with a hydrogen ion; thus the hydroxide ion must have a large proton-affinity, since water is scarcely dissociated. The electron-affinities of groups may be inferred from their influence on the strengths of acids and bases (Lewis), their effect on the mobility of tautomeric systems (Ingold, Shoppee, and Thorpe, J., 1926, 1427), their orienting action in additions (Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, 47, 1459) and substitutions (compare *Ann. Reports*, 1926, 129), and their effect on the dipole moments of molecules (compare *loc. cit.*). The hypothesis was tested in Part IV through the theoretical deduction that sulphonamides on *alkaline* hydrolysis ought to yield, not the normal sulphonic acid and amine, but a sulphinic acid (*i.e.*, sulphinate ion) and an imine, provided that the electron-affinity of R is sufficient.



$$\overset{\delta+\text{H}\cdots\cdots\text{OH}^{\ominus}}{\text{R}\leftarrow\text{CH}}\text{—NMe}\,|\,\text{—}\overset{+-}{\text{S}}\text{O}_2\cdot\text{C}_7\text{H}_7 \longrightarrow \text{R—CH}{=}\text{NMe} + \overset{\text{H}_2\text{O}}{}\text{SO}_2\cdot\text{C}_7\text{H}_7^{\ominus}$$

A consideration of the strengths as acids or bases of such compounds as phenol and aniline suggests that the phenyl group can exert a moderate electron-attraction, and in the case $R = C_6H_5$ the above anomalous mode of hydrolysis was realised. The direction of the disruption in this and all similar cases is determined by the circumstance that, as the hydroxide ion draws off the proton, so the electrons relieved from its attraction move towards the positively charged (sulphur) atom.

The application to the decomposition of quaternary ammonium hydroxides is obvious: the positive pole to which the liberated electrons move is the ammonium nitrogen atom, and it is unnecessary to add an alkali because the compound contains its own hydroxide ions:



$$\overset{\delta+\text{H}\cdots\cdots\cdots\cdots\text{OH}^-}{\text{R}\leftarrow\underset{\beta}{\text{CH}}\text{—}\underset{\alpha}{\text{CH}_2}\text{—}\overset{+}{\text{N}}\text{R}'_3} \longrightarrow \text{R—CH}{=}\text{CH}_2 + \text{NR}'_3 + \text{H}_2\text{O}$$

We may now consider how this hypothesis applies to the four points mentioned at the outset.*

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* It is not attempted to distinguish between the possible variations of the general mechanism, *e.g.*, possible lack of complete synchronisation of the electron transfers. The intention is to present only a preliminary survey of the field; each of the aspects thus outlined will be made the subject of a future, more detailed communication.

(1) The only alternative to the view that a β-hydrogen atom enters into the constitution of the eliminated water molecule is that one of the α-hydrogen atoms is first removed, the bivalent-carbon compound (sextet) so formed undergoing rearrangement:

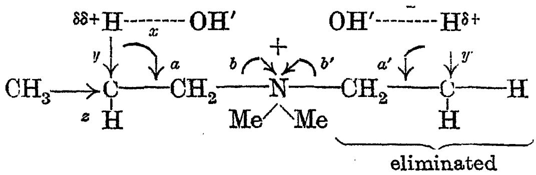
$$\{CH_3{\cdot}CH_2{\cdot}NR_3\}^{\cdot}\,OH' \longrightarrow CH_3{\cdot}CH\colon \longrightarrow CH_2{:}CH_2$$

There are many arguments against this theory; *e.g.*, ethylene has never been detected amongst the decomposition products of tetramethylammonium hydroxide, nor has stilbene been obtained from benzyltrimethylammonium hydroxide; yet these products would be expected to appear if a bivalent carbon compound intervened. Positive evidence against the rearrangement theory is provided by the observation that alkyltrimethylammonium hydroxides, which have no α-hydrogen atoms, decompose in the normal manner (Kohn, Schlegl, and Morgenstern, *Monatsh.*, 1907, **28**, 491, 525; compare p. 1004):

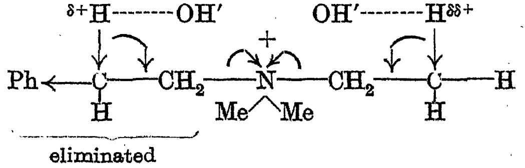
$$\{R{\cdot}CH_2{\cdot}CMe_2{\cdot}NMe_3\}^{\cdot}\,OH' \longrightarrow R{\cdot}CH{:}CMe_2 + NMe_3 + H_2O$$

Therefore it seems certain that it is one of the β-hydrogen atoms which is originally eliminated; and the mechanism suggested necessitates the direct abstraction of this hydrogen atom, since the removal of no other would enable the mutually accommodating *integral* electron displacements to occur with preservation of the octets.

(2) The rule that ethylene is eliminated in preference to any higher unsaturated hydrocarbon in quaternary ammonium hydroxide distillations is one to which we cannot call to mind any recorded exception. It is true that, as in Hofmann's original instances, *e.g.*, amyltriethylammonium hydroxide, most of the examples by which the rule has been illustrated are affected by the circumstance that several ethyl groups were present in the ammonium compound, which might therefore be predisposed to eliminate ethylene owing to statistical factors. This is not so, however, in the case of *dimethylethyl*-n-*propylammonium hydroxide*, which, as we have found, also yields mainly ethylene, and only a very little propylene. This is in agreement with the foregoing hypothesis; for, since alkyl groups repel their shared electrons more than does hydrogen (Lucas), the terminal methyl group of the propyl chain will reduce (z) the incipient ionisation (y) of the propyl β-hydrogen atom below that (y') of the ethyl β-hydrogen atom. That is to say, the extraction of the propyl proton by a hydroxide ion (x, y), and the dependent decomposition (a, b), will be hindered relatively to the extraction of the ethyl proton (x', y') and its dependent decomposition (a', b'):



Similarly, it follows that dimethyl-*n*-propyl-*n*-butylammonium hydroxide should yield more propylene than butylene, that dimethyl-*n*-butyl-*iso*butylammonium hydroxide should give *n*-butylene, and not *iso*butylene, as the main olefinic product; many similar predictions may be made; it is also clear that the only reason why no exception has previously been found to the Hofmann rule is that the groups with which ethyl has been placed in competition have hitherto all been of one type, namely, $-CH_2{\cdot}CH_2R$ or $-CH_2{\cdot}CHR_2$, where R has a smaller electron-affinity than hydrogen. Hence, if R were phenyl, the rule should be disobeyed—a deduction we have tested and found correct:



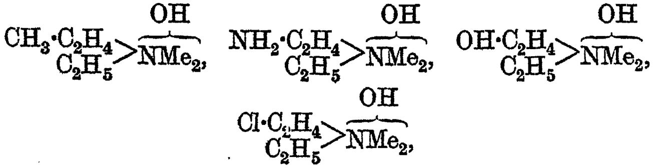
Again, a β-*p*-nitrophenylethyl group should be more readily eliminated as olefin than an unsubstituted β-phenylethyl group, and this also we have verified.

Thus it is possible to construct a series representing the relative ease of elimination of groups as olefins, and the sequence established by the above experiments,

$$CH_3{\cdot}CH_2{\cdot}CH_2 < H{\cdot}CH_2{\cdot}CH_2 < C_6H_5{\cdot}CH_2{\cdot}CH_2 < NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2,$$

could, of course, be filled in with many other groups from theoretical considerations. It should also be emphasised that such a series indicates not only the direction of a particular decomposition, but also the ease with which it will take place. Thus we found that decompositions resulting in the elimination of propylene or ethylene always required a fairly high temperature, whereas that which gave styrene occurred in hot dilute aqueous solution, and that which yielded *p*-nitrostyrene took place during the attempted preparation of the quaternary compound, which we were unable to isolate for this reason.

One more example may be given. From the probable increasing electron-affinity of the groups in the series CH_3, NH_2, OH, Cl—as indicated, for example, by the increasing proportion of *m*-substitution in $CH_3\cdot COPh$, $NH_2\cdot COPh$, $OH\cdot COPh$, $Cl\cdot COPh$ (Cooper and Ingold, this vol., p. 836)—it follows that the ammonium hydroxides



$$\begin{matrix}CH_3\cdot C_2H_4\\ C_2H_5\end{matrix}\!>\overbrace{NMe_2}^{OH},\quad \begin{matrix}NH_2\cdot C_2H_4\\ C_2H_5\end{matrix}\!>\overbrace{NMe_2}^{OH},\quad \begin{matrix}OH\cdot C_2H_4\\ C_2H_5\end{matrix}\!>\overbrace{NMe_2}^{OH},\quad \begin{matrix}Cl\cdot C_2H_4\\ C_2H_5\end{matrix}\!>\overbrace{NMe_2}^{OH},$$

should yield successively diminishing proportions of ethylene and increasing proportions of dimethylethylamine on decomposition. This appears to be the case. The main products obtained from the first compound are ethylene and dimethylpropylamine; the second gives corresponding principal products ethylene and β-aminoethyldimethylamine, but in addition yields acetaldehyde (evidently derived from vinylamine) and an appreciable quantity of dimethylethylamine; the third compound of the series yields still less ethylene, and appears to give more acetaldehyde (vinyl alcohol), and nearly equal amounts of dimethylethylamine and β-hydroxyethyldimethylamine; finally, the chloro-compound yields no appreciable quantity of ethylene, but gives a basic product consisting mainly of dimethylethylamine—another exception to Hofmann's rule.

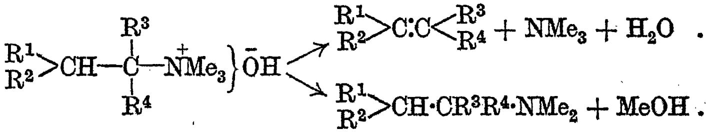
It will be evident from these examples that the decomposition of quaternary ammonium hydroxides furnishes a means of comparing electron-affinities which should be capable of many applications.

(3) In the above examples, the ammonium atom achieves neutrality by the appropriation of electrons which become available as a direct consequence of the withdrawal of a β-hydrion from one of the alkyl groups. It may happen, however, (i) that this mechanism cannot function owing to the absence of β-hydrogen atoms, (ii) that it either cannot function, or can do so only with great difficulty, owing to the more or less effective stabilisation of all the existing β-protons by the strong electron-repulsion of neighbouring groups. In these cases, the only other means open to the nitrogen atom is to extract the shared electrons from a group without the independent facilitation of a compensating supply of electrons for the depleted carbon atom; in this event, the group is ejected as a positive ion, which will at once unite with any negative ion that happens to be present in the liquid, so that in the decompositions now under consideration it appears as an alcohol (compare following section):

$$R'R''R'''\overset{+}{N}\overset{\curvearrowleft}{\text{——}}R + \overset{-}{OH} = R'R''R'''N + \overset{+}{R} + \overset{-}{OH} = R'R''R'''N + R\cdot OH.$$

Which of the four groups will thus be eliminated, and the facility of the process, will depend on the relative stabilities of the possible positive ions, and these in turn can be inferred, for example, from the reactivities of the iodides RI, R′I, R″I, R‴I towards the same ionising substance. Thus, amongst the commoner groups devoid of an available β-hydrogen atom the order of ease of elimination should be $Ph_3C > Ph_2CH > PhCH_2 > CH_3 > Ph$, and this has been confirmed for the last three groups by Collie and Schryver (J., 1890, **57**, 767), who found that benzyltrimethylammonium hydroxide yielded benzyl alcohol, whilst phenyltrimethylammonium hydroxide gave methyl alcohol on distillation.

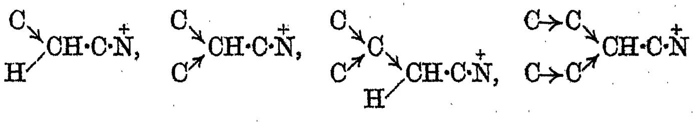
In considering the relative ease of elimination of any *one* group as alcohol from various ammonium hydroxides which can also yield an olefin, we may take for illustration the elimination of methyl alcohol, since this is the case which usually arises in exhaustive methylations. If the quaternary hydroxide is of the form $\{AlkNMe_3\}^{\cdot}OH'$, the possible decompositions are:



$$\left.\begin{matrix}R^1\\R^2\end{matrix}\right>CH{-}\overset{R^3}{\underset{R^4}{C}}{-}\overset{+}{N}Me_3\Big\}\bar{O}H \rightarrow \left.\begin{matrix}R^1\\R^2\end{matrix}\right>C{:}C\left<\begin{matrix}R^3\\R^4\end{matrix}\right. + NMe_3 + H_2O \quad . \quad (A)$$

$$\rightarrow \left.\begin{matrix}R^1\\R^2\end{matrix}\right>CH{\cdot}CR^3R^4{\cdot}NMe_2 + MeOH \quad . \quad (B)$$

Now since (B) takes place only when (A) is inhibited, it follows that the occurrence of (B) depends primarily on the electron-repulsion of R^1 and R^2; it will depend only to a small extent on the groups R^3 and R^4, because any electronic strain set up by these radicals can reach the β-hydrogen atom only indirectly. From a consideration of strain-paths such as



it can be seen that the order of the effects due to alkyl groups R^1 and R^2 should be: $CH_3{\cdot}[CH_2]_n > CH_3{\cdot}[CH_2]_{n-1} > \ldots\ldots > CH_3 > H$; and $(CH_3)_2 > CH_3{\cdot}CH_2$, $(CH_3)_2CH > CH_3{\cdot}[CH_2]_2$, etc.; or, in words, longer chains should be more effective than shorter, and branched chains more effective than isomeric normal chains. Also it would be expected that the effect of the more remote parts of long chains would be small in comparison with that of the portions nearer the β-hydrogen atom.

The following table shows how far these conclusions are supported by experimental data relating to the effect of alkyl groups on the elimination of methyl alcohol from hydroxides of the type $\{AlkNMe_3\}^{\cdot}OH'$.

Decomposition of Trimethylalkylammonium Hydroxides.

No.	Alkyl group.	R^1.	R^2.	R^3.	R^4.	Reaction B (%).
1	Ethyl.	H	H	H	H	0
2	*iso*Propyl.	H	H	CH_3	H	0
3	*sec.*-Butyl.	H	H	$CH_3{\cdot}CH_2$	H	Small.
4	*sec.*-Amyl.	H	H	$CH_3{\cdot}CH_2{\cdot}CH_2$	H	Small.
5	*tert.*-Butyl.	H	H	CH_3	CH_3	Small.
6	*n*-Propyl.	CH_3	H	H	H	19
7	*n*-Butyl.	$CH_3{\cdot}CH_2$	H	H	H	25
8	*iso*Butyl	CH_3	CH_3	H	H	37
9	β-Ethyl-*n*-butyl.	$CH_3{\cdot}CH_2$	$CH_3{\cdot}CH_2$	H	H	57
10	β-*n*-Propyl-*n*-amyl.	$CH_3{\cdot}CH_2{\cdot}CH_2$	$CH_3{\cdot}CH_2{\cdot}CH_2$	H	H	69

The figures for examples (1) and (2) are taken from Collie and Schryver's published results; the experimental basis for the remainder is recorded in this paper, but example (6) was investigated also by Collie and Schryver, whose observations accord with the figure given. In addition to these results, data have been recorded by von Braun (*Annalen*, 1911, **382**, 1) which appear to establish the anticipated sequence of alkyl groups :

n-Butyl<*n*-Amyl<*n*-Hexyl<*n*-Heptyl, *n*-Octyl, ... *n*-Cetyl

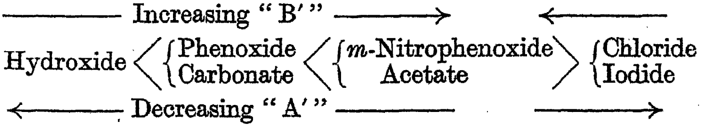
but these are not included in the table, because, although they are in the correct order relatively, we doubt their essential accuracy : certainly, von Braun's results for trimethyl-*n*-butylammonium hydroxide differ widely from ours, and it is proposed to reinvestigate the other cases. In the meantime it is quite clear (i) that β-alkyl substituents (R^1, R^2) are more effective than α-alkyl groups (R^3, R^4) in promoting reaction B, (ii) that the rule for normal chains holds at least for the lower members: $H < CH_3 < C_2H_5 < C_3H_7$, and (iii) that a comparison of the *n*- and *iso*butyl-compounds exemplifies the predicted effect due to the branching of carbon chains.

(4) It follows from the basic hypothesis that the ease of removal of the β-proton (reaction A) depends (*a*) on its vulnerability, (*b*) on the proton-avidity of the attacking anion. Factor (*a*) has been discussed (Section 3); now it is necessary to consider factor (*b*).

In order to maintain factor (*a*) constant, we must consider a *single* ammonium ion, and the example chosen for experimental study was No. 6 in the table. Now a precise measure of the proton-affinity of an attacking anion X′ would be available if the electrolytic dissociation constant of the compound $HX(\rightleftharpoons H^{\cdot} + X')$ under the conditions of the decomposition (*i.e.*, in the fused material) were known. Such data, however, are not available, and in their absence the most acceptable criterion is the dissociation constant in water or some other solvent. Adopting this view, and remembering that it may possibly lead to anomalies, since the relative strengths of electrolytes are known to be sometimes inverted on passing from non-aqueous solvents to water, it follows that reaction (A′) might be successively inhibited and (B′) correspondingly favoured on passing through such a series as the quaternary hydroxide, phenoxide, nitrophenoxide, chloride; thus, since the hydroxide gives 19% of methyl alcohol, the phenoxide should yield a greater proportion of anisole, and a nitrophenoxide still more nitroanisole, for phenol is a stronger acid than water, and the nitrophenols are stronger than phenol.

$$\left.\mathrm{C_3H_7{\cdot}\overset{+}{N}Me_3}\right\}\overset{-}{\mathrm{X}}\begin{array}{l}\nearrow \mathrm{C_3H_6 + NMe_3 + HX} \quad . \quad . \quad . \quad \text{(A}'\text{)}\\ \searrow \mathrm{C_3H_7{\cdot}NMe_2 + MeX} \quad . \quad . \quad . \quad \text{(B}'\text{)}\end{array}$$

Actually our yields of anisole and *m*-nitroanisole were 65% and 89% respectively, and experiment establishes the following relationships amongst trimethyl-*n*-propylammonium hydroxide and six of its salts.



The first five substances are thus related in accordance with the tentative prediction based on aqueous acid-strengths, but the halogen salts are anomalous, since they give slightly more olefin than the nitrophenoxide or acetate. There is, however, nothing demonstrably inconsistent with the general theory in this behaviour, because the halogen acids are known to be almost wholly undissociated in most non-aqueous solvents, and it is not impossible that under the conditions of the decompositions hydrogen chloride and hydrogen iodide may be weaker acids than acetic acid.* The other conceivable source of disturbance, namely, the effect of the anions in directly facilitating the removal of the positive alkyl ions, we do not regard as likely to produce large irregularities, since, owing to the protection of the positive carbon nucleus by its surrounding shell of electrons, the direct attraction between that nucleus and any circumambient anions would presumably be relatively feeble.

EXPERIMENTAL.

(I). *Dimethylethyl*-n-*propylammonium Hydroxide*.—A modification of Eschweiler's method (*Ber*., 1905, **38**, 881) was used for the preparation of dimethylethylamine. The solution obtained by neutralising 13·5 c.c. of 33% aqueous ethylamine with hydrochloric acid was evaporated to a paste, which was then heated with 38% formaldehyde (20 c.c.) under pressure at 140—150° for 3—4 hours. The product of several such experiments was evaporated to a paste, which was treated with solid potassium hydroxide, the evolved bases, b. p. 30—40° (the greater part had b. p. 36°), being collected in well-cooled ether. The dimethylethylamine thus obtained was not pure, since it gave a non-crystalline quaternary iodide with *n*-propyl iodide. The tertiary base was therefore converted into its picrate with benzene–ethereal picric acid, and the salt crystallised from alcohol until its m. p. rose to and remained constant at 200—201°. The pure picrate was converted into the hydrochloride by shaking a suspension in hydrochloric acid with benzene; the free base, b. p. 36—38°, was then liberated.

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* Hydrogen chloride is a non-conductor of electricity, but solutions of acetic acid in hydrogen chloride are good conductors (Archibald, *J. Amer. Chem. Soc.*, 1907, **29**, 1471).

The following method also was used. Well-dried ethylamine hydrochloride, prepared from 120 g. of 33% aqueous ethylamine, was thoroughly mixed with 90 g. of paraformaldehyde and heated under reflux for 2·5 hours at 135° (internal temperature). The product was covered with ether and decomposed with concentrated aqueous sodium hydroxide, and the ethereal solution of the base (it is undesirable to extract more than once with ether) was precipitated with ethereal picric acid (150 g.). The picrate was collected from the still warm suspension (the salt which subsequently separates being very impure), crystallised twice from water to remove a sparingly soluble oily product, converted into the hydrochloride and thence into the free base (yield, 25 g.).

A mixture of this (19 g.) with *n*-propyl iodide (50 g.) was kept for 4 days at the ordinary temperature, and the hygroscopic *dimethylethyl*-n-*propylammonium iodide* thus obtained was converted into the *picrate* by treatment with saturated aqueous sodium picrate. This salt separates from alcohol or water in orange-yellow needles or tablets, m. p. 185—187° (Found: C, 45·55; H, 6·0. $C_{13}H_{20}O_7N_4$ requires C, 45·35; H, 5·8%).

Decomposition of dimethylethyl-n-*propylammonium hydroxide.* A solution of this substance prepared from the iodide, silver oxide, and water was distilled through four wash-flasks. The first two contained 3*N*-hydrochloric acid, and the second two bromine, the first, third, and fourth being cooled in ice-water. Usually the decomposition products were completely trapped in the first and the third vessel.

Methyl alcohol was detected by distilling the hydrochloric acid solution and treating the first portion of the distillate with *p*-nitrobenzoyl chloride and alkali; a small amount of methyl *p*-nitrobenzoate, m. p. 92°, was then formed.

The olefin bromide, obtained after destruction of the excess of bromine with freshly prepared sodium hydrogen sulphite, boiled completely at 131—132° (ethylene dibromide has b. p. 131°, propylene dibromide has b. p. 140°) and therefore consisted mainly of ethylene dibromide (Found: C, 13·2; H, 2·3%). The material was fractionally distilled, and analysis of the last few drops, b. p. about 132° (Found: C, 15·5, 15·2; H, 2·3, 2·35; Br, 82·1, 82·3. Calc. for $C_2H_4Br_2$: C, 12·8; H, 2·1; Br, 85·1. Calc. for $C_3H_6Br_2$: C, 17·8; H, 3·0; Br, 79·2%) showed that some propylene dibromide was present.

Confirmatory results were obtained on examining the basic decomposition products, which were first converted into their picrates. Analysis of the crude mixture indicated *dimethyl*-n-*propylammonium picrate* to be the principal constituent (Found: C, 41·9, 41·7; H, 4·9, 5·1. $C_{11}H_{16}O_7N_4$ requires C, 41·8; H, 5·1%), and 70% of this substance was readily isolated in stout, lemon-yellow prisms, m. p. 108—109°, by crystallisation from ethyl acetate (Found: C, 41·9; H, 5·4%). It was identified by conversion into trimethyl-*n*-propylammonium picrate, m. p. 195° (below). The residue was repeatedly fractionally crystallised from toluene and ethyl acetate, used for the most part alternately; besides a further quantity of dimethyl-*n*-propylammonium picrate, a small amount of dimethylethylammonium picrate (identified by mixed m. p.) was thus obtained, together with a residue which may have contained methylethylpropylammonium picrate, although we did not succeed in isolating this.

The hydroxide therefore decomposes mainly into dimethylpropylamine and ethylene, to a small extent into dimethylethylamine and propylene, and also to a slight extent into methyl alcohol and, presumably, methylethylpropylamine. This seems to be the first recorded instance of the formation of methyl alcohol in the decomposition of a quaternary ammonium hydroxide which also yields ethylene.

(II). β-*Phenylethyldimethylethylammonium Hydroxide.*—β-Phenylethyldimethylamine (Goss, Hanhart, and Ingold, this vol., p. 250) liberated from 28 g. of the picrate was warmed with a benzene solution of ethyl iodide (20 g.) for 2 hours on the water-bath. The *iodide* was collected (22 g.) and crystallised twice from alcohol–ethyl acetate; m. p. 158—159°. It is easily soluble in water, alcohol, and chloroform (Found: C, 47·5; H, 6·9. $C_{12}H_{20}NI$ requires C, 47·2; H, 6·6%).

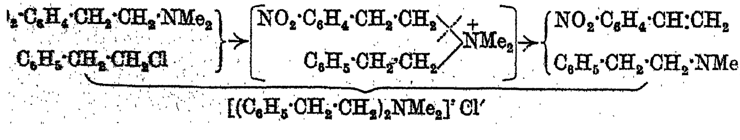
The *picrate* appears to form two crystallographic modifications. The precipitate obtained by adding sodium picrate solution to an aqueous solution of the iodide melts at about 113°, and on crystallisation from alcohol forms well-defined, lemon-yellow needles, m. p.

96—97°. If, however, the needles are mixed with a trace of the crude product the m. p. is 115—116°, and if the melt obtained by heating the needles to just above 97° is treated with a "speck" of the crude powder, solidification at once occurs and the product then melts at 115—116°. The needles are only slightly soluble in cold ethyl alcohol, but are readily soluble in acetone (Found: C, 53·5; H, 5·6. $C_{18}H_{22}O_7N_4$ requires C, 53·2; H, 5·4%).

Decomposition of β-*phenylethyldimethylethylammonium hydroxide.* The aqueous solution of the hydroxide, prepared from the iodide and an aqueous suspension of silver oxide, began to decompose at 100°. The products were exclusively styrene and dimethylethylamine, both of which were isolated in the pure condition in excellent yield. The former, b. p. 140—143°, was characterised through its dibromide, m. p. 74°, which was compared with an authentic specimen. The latter was converted into its picrate, which formed large, lustrous, yellow leaves, m. p. 202—203° (not needle-like crystals, m. p. 193—194°, as described by Kohn and Morgenstern, *Monatsh.*, 1907, **28**, 496), and was identified by direct comparison and by analysis (Found: C, 40·0; H, 4·6. Calc.: C, 39·7; H, 4·6%).

In order to detect any decomposition in the direction leading to ethylene and β-phenylethyldimethylamine, a portion of the basic product was oxidised with permanganate under conditions in which this base yields benzoic acid quantitatively (Goss, Hanhart, and Ingold, *loc. cit.*). Benzoic acid was not obtained, and an experiment designed to detect the evolution of small amounts of ethylene also yielded a negative result.

(III). *Attempted Preparation of* p-*Nitrodi*(β-*phenylethyl*)*dimethylammonium Chloride from* β-*Phenylethyl Chloride and* p-*Nitro*-β-*phenylethyldimethylamine*; *Formation of* p-*Nitrostyrene*, β-*Phenylethyldimethylamine and Di*(β-*phenylethyl*)*dimethylammonium Chloride.*—We regard these experiments as showing that the *p*-nitrodi(β-phenylethyl)dimethylammonium ion is unstable under the experimental conditions owing to the great tendency to the elimination of the *p*-nitrophenylethyl group as nitrostyrene. The only quaternary salt which could be isolated from the product of interaction of β-phenylethyl chloride and *p*-nitro-β-phenylethyldimethylamine was di(β-phenylethyl)dimethylammonium chloride, the formation of which we explain as follows:



$$\left.\begin{matrix} {}_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2 \\ C_6H_5\cdot CH_2\cdot CH_2Cl \end{matrix}\right\} \rightarrow \left[\begin{matrix} NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2 \\ C_6H_5\cdot CH_2\cdot CH_2 \end{matrix} \!>\! \overset{+}{N}Me_2\right] \rightarrow \left\{\begin{matrix} NO_2\cdot C_6H_4\cdot CH{:}CH_2 \\ C_6H_5\cdot CH_2\cdot CH_2\cdot NMe_2 \end{matrix}\right.$$

$$[(C_6H_5\cdot CH_2\cdot CH_2)_2NMe_2]^{\cdot}\,Cl'$$

Experiments were carried out under various conditions, but with substantially identical results; the following is typical.

p-Nitro-β-phenylethyldimethylamine, liberated from 20 g. of the pure oxalate, was heated with a slight excess of β-phenylethyl chloride for 48 hours on the water-bath, and the partly solid reaction product was shaken with water and ether. The ethereal layer contained no bases, but only an olefinic substance together with the excess of β-phenylethyl chloride. The residue obtained on evaporation was treated with bromine, and the solid dibromide identified as *p*-nitrostyrene dibromide by direct comparison with a genuine specimen and by oxidation by means of permanganate to *p*-nitrobenzoic acid. No styrene dibromide could be found.

The aqueous solution was basified and extracted with ether, and the ethereal solution precipitated by picric acid dissolved in benzene. The picrates (10 g.) consisted of a mixture of β-phenylethyldimethylammonium picrate (about one-third) and *p*-nitro-β-phenylethyldimethylammonium picrate (about two-thirds), which were readily separated by crystallisation from alcohol containing 10% of acetone, the former salt remaining in the solution.

The alkaline aqueous solution was filtered, neutralised, and precipitated with aqueous sodium picrate; the crude *di*(β-*phenylethyl*)*dimethylammonium picrate* thus obtained crystallised from alcohol in orange-yellow plates (8 g.), m. p. 111—112° (Found: C, 60·5; H, 5·4; N, 11·8. $C_{24}H_{26}O_7N_4$ requires C, 59·8; H, 5·4; N, 11·6%). This compound was also prepared by heating 33% alcoholic dimethylamine solution with excess of β-phenylethyl chloride in a sealed tube at 90° for 16 hours. The *hydrochloride* was thus obtained in good yield. It is readily soluble in water, alcohol, acetone, and chloroform, and separates from the last or from acetone–benzene in colourless needles, m. p. 70°. It is insoluble in ether and benzene and is not hygroscopic. On treatment with sodium picrate solution the above picrate is formed.

Decomposition of di(β-*phenylethyl*)*dimethylammonium hydroxide*. An aqueous solution of the hydroxide rapidly decomposed when boiled, the products being styrene, which was identified as its bromide, and β-phenylethyldimethylamine, identified as picrate.

β-*p*-Nitrophenylethyldimethylamine was prepared by heating β-*p*-nitrophenylethylamine hydrochloride (9 g.) with 20 c.c. of 40% formaldehyde under pressure at 135°. The chloride thus obtained was converted into the oxalate, which was twice crystallised from 95% alcohol (yield of pure oxalate, 10·5 g.). The more rapid but less economical method of heating the primary hydrochloride (2 parts) with paraformaldehyde (1 part) for 1 hour in an open flask at 150° was also employed; complex condensation products were formed which impaired the yield.

(IV). β-*Aminodimethyldiethylammonium Hydroxide,* β-*Dimethylaminodimethyldiethylammonium Hydroxide,* s-*Tetramethyldiethylethylenediammonium Dihydroxide, Hexamethylethylenediammonium Dihydroxide, and their Intermediates.*—The first of these bases, $(NH_2\cdot CH_2\cdot CH_2\cdot NMe_2Et)^{\cdot}OH'$, was prepared by hydrolysis of the condensation product, $\{C_6H_4{:}(CO)_2{:}N\cdot CH_2\cdot CH_2\cdot NMe_2Et\}^{\cdot}Br'$, of phthal-β-bromoethylimide and dimethylethylamine.

Phthal-β-bromoethylimide (10 g.), absolute alcohol (15 c.c.), and 25% alcoholic dimethylethylamine (11 g. of solution) were warmed together in a sealed tube with frequent shaking until a homogeneous liquid resulted. The tube was then heated for 6 hours at 120°, and opened while still warm, since, on cooling, a very stiff cake of crystals is obtained. After being washed with absolute alcohol, the β-*phthalimidodimethyldiethylammonium bromide* was almost pure, m. p. 280° (decomp.); the yield (about 60%) could be slightly increased by working up the alcoholic filtrate. The salt is extremely soluble in water and is conveniently crystallised by dissolving it in a little water, warming, and adding much absolute alcohol; it then separates in pearly leaflets (Found: C, 51·4; H, 6·2. $C_{14}H_{19}O_2N_2Br$ requires C, 51·4; H, 5·8%).

The bromide was boiled with 20% hydrochloric acid (6 parts) for 6 hours and the cooled solution was filtered from phthalic acid and evaporated to dryness. A solution of the residue in a little water was filtered from a small quantity of phthalic acid and treated with sodium picrate solution. *Dimethylethylethylenediammonium dipicrate,* $\{NH_3\cdot CH_2\cdot CH_2\cdot NMe_2Et\}^{\cdot\cdot}\{O\cdot C_6H_2(NO_2)_3\}'_2$, separates from hot water in well-formed, lemon-yellow leaflets, m. p. 198° (decomp.) (Found: C, 37·3; H, 4·1. $C_{18}H_{22}O_{14}N_8$ requires C, 37·6; H, 3·8%).

Tetramethylethylenediamine has been prepared by Freund and Michaels (*Ber.*, 1897, **30**, 1385) from ethylene dibromide and dimethylamine. The bromide (14 g.) and the base (20 g. of a 33% alcoholic solution) were heated for 3 hours at 100° under pressure, and the salt was washed with alcohol and distilled with potassium hydroxide. The base was dried by distillations over potassium hydroxide and barium oxide (yield 5·6 g.).

Attempts to prepare the same compound by methylating ethylenediamine with paraformaldehyde were unsuccessful when free ethylenediamine or its hydrochloride was used, but succeeded with the sulphate. The yield is only 40%, but the method is rapid and convenient. A solution of ethylenediamine (40 g.) in absolute alcohol was neutralised with concentrated sulphuric acid and the precipitated salt was collected and dried. An intimate mixture of this with paraformaldehyde (90 g.) was heated under reflux, melting and frothing commencing at 90°. The internal temperature was maintained between 130° and 140° for 4 hours. After cooling, the product was mixed with concentrated aqueous potassium hydroxide and distilled (b. p. about 95°), and the distillate was dried with solid potassium hydroxide and distilled over barium oxide; the main portion boiled at 121—122·5°. The dipicrate is sparingly soluble, but separates from aqueous acetone in yellow needles, m. p. 263° (decomp., becoming brown at 250°) (Knorr, *Ber.*, 1904, **37**, 3509, gives 252° as the m. p. of an unrecrystallised specimen).

An ethereal solution of tetramethylethylenediamine was allowed to react with ethyl iodide (1 mol.) for several days. Small white needles, a liquid, and large needles were successively deposited. The precipitate was washed with ether by decantation, exposed in a desiccator until completely solid, and then crystallised from hot alcohol. s-*Tetramethyldiethylethylenediammonium di-iodide* separated in large, colourless needles, which lost their lustre in a desiccator or in air; m. p. 233° (decomp.) (Found: C, 28·1; H, 6·4. $C_{10}H_{26}N_2I_2$ requires C, 28·0; H, 6·1%). The salt is readily soluble in water and gives a neutral reaction. On addition of aqueous sodium picrate, the *dipicrate* is precipitated, which separates from aqueous acetone–alcohol in small, flattened needles, m. p. 261° (decomp.) (Found: C, 42·2; H, 4·9. $C_{22}H_{30}O_{14}N_8$ requires C, 41·9; H, 4·7%).

The alcoholic filtrate obtained in the preparation of the diiodide was evaporated in a vacuum to a thick syrup, which had a strongly alkaline reaction and was soluble in chloroform. Its solution in alcohol was mixed with alcoholic hydrogen chloride and the pale brown hygroscopic salt was collected and converted into the picrate, which, after crystallisation from aqueous acetone–alcohol, had m. p. 212—214°. The same picrate was obtained when tetramethylethylenediamine was allowed to react with a small quantity of ethyl iodide without a solvent for 48 hours at the ordinary temperature. The solid iodide, which was collected and washed with ether, was hygroscopic and its aqueous solution had an alkaline reaction. The addition of aqueous sodium picrate yielded a precipitate having m. p. 210—214°. A similar but less pure product, m. p. 207—214°, was obtained in small amount, along with a large quantity of the diammonium iodide, m. p. 233°, when excess of ethyl iodide was employed. The m. p. (212—214°) of β-*dimethylaminodimethyldiethylammonium picrate* is depressed to about 205° by admixture with the dipicrate (m. p. 261°), but analysis indicates the presence of a small amount of this salt which we were unable to remove (Found: C, 44·6; H, 5·8. $C_{14}H_{23}O_7N_5$ requires C, 45·0; H, 6·2%).

Hexamethylethylenediammonium dipicrate, orange-yellow needles, m. p. 285° (decomp.), was prepared by mixing tetramethylethylenediamine with trinitroanisole (2 mols.) in benzene solution. It was crystallised from a large volume of hot water (Found: C, 40·1; H, 4·4. $C_{20}H_{26}O_{14}N_8$ requires C, 39·9; H, 4·3%).

Decomposition of β-*aminodimethyldiethylammonium hydroxide.* The aqueous solution obtained by shaking a suspension of the picrate in hydrochloric acid with benzene was concentrated to a syrup, diluted, and decomposed with water and excess of silver oxide; the filtered solution was then distilled in the usual apparatus. A portion of the solution in the 3*N*-hydrochloric acid trap was distilled and the first fraction of distillate, which strongly reduced Fehling's solution, was treated with *p*-nitrophenylhydrazine, acetaldehyde-*p*-nitrophenylhydrazone being obtained.

The solution in the bromine trap was mixed with ice, decolorised with sulphur dioxide, rendered alkaline, and extracted with light petroleum; ethylene dibromide, b. p. 131°, was then obtained in 45% yield (Found: C, 12·9; H, 2·3; Br, 84·9. Calc.: C, 12·8; H, 2·1; Br, 85·1%).

The acid solutions were evaporated to dryness and the hygroscopic residue was mixed with solid potassium hydroxide and distilled at 60°. The distillate was collected in ether and treated with picric acid in benzene, and the precipitate was crystallised twice from alcohol, pure dimethylethylammonium picrate being obtained (yield 19%). The residual bases were then completely distilled and boiled with alcoholic methyl sulphate and anhydrous sodium carbonate for 2 hours. On adding water, boiling off the alcohol, and adding sodium picrate solution in excess, a precipitate was obtained which, after two crystallisations from boiling water, yielded pure hexamethylethylenediammonium dipicrate, identical with the specimen described above (yield 30%).

Decomposition of β-*dimethylaminodimethyldiethylammonium hydroxide.* The solution of the hydroxide was prepared and distilled as in the last example, and the ethylene dibromide (yield 48%) isolated in the same way. The bases were also worked up in a similar manner, excepting that the tetramethylethylenediamine was purified through its sparingly soluble picrate and was not converted into the quaternary compound. The yield of dimethylethylammonium picrate was 20% and of the diammonium dipicrate 28%.

(V). β-*Hydroxydimethyldiethylammonium Hydroxide.*—β-Hydroxydimethylethylamine was prepared by a modification of Knorr and

Matthes's method (*Ber.*, 1901, **34**, 3482). Ethylene oxide (20 g.) was added to 64 g. of 33% aqueous dimethylamine previously diluted with ice-water. The product was distilled, the first 20 c.c. being rejected, up to 136°, and the distillate was saturated with potassium hydroxide and extracted with ether. The extract was dried with sodium sulphate and with solid potassium hydroxide, and the ether distilled up to 40°. Barium oxide was then added, and the aminohydrin distilled, b. p. 130—133°.

The reaction with ethyl iodide takes place on warming in ethereal solution, the product separating in colourless needles, which may be accompanied by a viscous liquid if the hydroxy-base used is not perfectly dry. In the latter case the liquid product may be caused to solidify by desiccation. β-*Hydroxydimethyldiethylammonium iodide* is excessively soluble in water and alcohol and is very hygroscopic. The *picrate* separates from water or alcohol in long needles, m. p. 237—239°. It is easily soluble in hot water and alcohol and very easily soluble in acetone (Found: C, 42·0; H, 5·2; N, 16·4. $C_{12}H_{18}O_8N_4$ requires C, 41·6; H, 5·2; N, 16·2%). It forms two modifications, the more stable having m. p. 258°.

Distillation of the hydroxide. The quaternary hydroxide prepared from the iodide and silver oxide was distilled as usual. Much frothing occurred. Acetaldehyde was identified through its *p*-nitrophenylhydrazone, as in Section IV, and ethylene as its dibromide (yield 37%). The acid solution was evaporated and the residue was covered with ether and basified with solid potassium hydroxide. The ethereal extract was dried with sodium sulphate and distilled over barium oxide. The main portion of the ethereal distillate, on treatment with a benzene solution of picric acid, yielded pure dimethylethylammonium picrate. The last portion, which was collected separately, on similar treatment gave a mixture of picrates (m. p. 190—195°) from which the same pure picrate (m. p. 202—203°) was obtained by crystallisation from alcohol (total yield, 26%). The β-hydroxydimethylethylamine passed over at about 100—135° and was purified through its picrate (Knorr and Matthes, *loc. cit.*).

(VI). β-*Chlorodimethyldiethylammonium Hydroxide.*—β-Chlorodimethylethylamine was prepared by Knorr (*loc. cit.*) by heating β-hydroxydimethylethylamine with fuming hydrochloric acid at 180°. The following process is less laborious.

A chloroform solution of β-hydroxydimethylethylamine, obtained from 30 g. of ethylene oxide as described in Section V, was well cooled and slowly treated with thionyl chloride until the two liquid layers at first produced became one. The solution was then heated under reflux, and the crystals, which commenced to separate after

15 minutes, were collected after the mixture had boiled for 2 hours and cooled. They were washed with a little chloroform and dried in a desiccator. In this way, 33 g. of almost pure β-chlorodimethylethylammonium chloride were obtained in colourless, hygroscopic needles, m. p. 200°. The thionyl chloride filtrate was distilled, and the brown mass of crystals was washed with ether and crystallised from a little absolute alcohol (yield, 6 g.; m. p. 196°). The corresponding *picrate* separated from 95% alcohol in large leaflets, m. p. 126—127° (Found: C, 36·1; H, 4·3. $C_{10}H_{13}O_7N_4Cl$ requires C, 35·7; H, 3·9%).

An aqueous solution of the above chloride (30 g.) was mixed with concentrated potassium hydroxide, and the base extracted with ether. Most of the ether was evaporated and the concentrated ethereal solution was warmed for several hours with excess of ethyl iodide. The crystalline product was extracted with hot alcohol, which left undissolved a small amount of tetramethylpiperazinium dichloride (m. p. 304°, decomp.), and the *β-chlorodimethyldiethylammonium iodide*, which separated, on cooling, in needles, m. p. 198° (Found: C, 27·2; H, 5·7. $C_6H_{15}NClI$ requires C, 27·3; H, 5·7%), was converted into the *picrate* by precipitation from aqueous solution with sodium picrate. This salt forms long, transparent, yellow needles, m. p. 192—193° (Found: C, 39·2; H, 4·8. $C_{12}H_{17}O_7N_4Cl$ requires C, 39·5; H, 4·7%).

Decomposition of β-chlorodimethyldiethylammonium hydroxide. The hydroxide appeared to be stable in boiling aqueous solution, but as soon as the water was driven off a violent reaction set in. The main basic product was dimethylethylamine, which was isolated as picrate in the usual way. Only traces of gaseous olefin were collected in the bromine, and in the distilling flask an amorphous product remained which contained chlorine and nitrogen but was insoluble in the usual solvents.

(VII). *Trimethyl-*n*-propylammonium Hydroxide.*—Collie and Schryver showed that the main products of decomposition were trimethylamine and propylene; analytical data indicated that dimethylpropylamine also was produced in small amount. The solution obtained by treating trimethyl-*n*-propylammonium iodide with silver oxide and water was concentrated by distillation (the distillate did not contain more than a trace of trimethylamine) and then distilled through the usual series of traps. The yields of methyl alcohol, isolated as methyl *p*-nitrobenzoate, ranged from 4 to 7%. Experiments with artificially prepared, dilute solutions of methyl alcohol showed that this method of isolation is by no means quantitative, and hence the amount of methyl alcohol formed must have been considerably greater than that stated above. Nearly pure propylene dibromide, b. p. 134—141°, the main part having b. p. 139—140° (Found: C, 18·1; H, 2·9; Br, 79·2. Calc.: C, 17·8; H, 3·0; Br, 79·2%), was obtained in 81% yield. Preliminary experiments showed that the absorption of the olefin was quantitative and took place entirely in the first bromine trap. After successive treatment with ice, sulphur dioxide and sodium hydroxide (slight excess), the bulk of the bromide was run off, and the remaining trace extracted with a little petroleum (b. p. 40—45°). The mixture of bromide and petroleum was dried with calcium chloride and distilled through a cooled column. The yield recorded above includes a correction (2·6%) for the weight of vapour filling the flask at the boiling point up to the level of the side arm. Our practice in this and similar experiments was to calculate this correction from the gas laws and also weigh the drop of liquid which condensed in the flask on cooling; usually both estimates agreed, but in the event of disagreement, the smaller value was regarded as the correction. A small correction is also applied for the volatility of the bromide in the ligroin vapour. The yield of mixed quaternary picrates obtained from the mixed bases and trinitroanisole was 89% (m. p. about 190°) and a single crystallisation from 95% alcohol yielded 78% (*i.e.*, 87·5% of the mixture) of pure tetramethylammonium picrate (Found: C, 40·4, 40·2; H, 4·7, 4·9; N, 18·5. Calc. for tetramethylammonium picrate: C, 39·7; H, 4·6; N, 18·5. Calc. for trimethylpropylammonium picrate: C, 43·7; H, 5·5; N, 17·0%). From the carbon content, the mixture contains 15% of trimethylpropylammonium picrate, *i.e.*, 14 molecules %, which agrees with the yield of propylene dibromide to within the limits of analytical accuracy. A small quantity of trimethylpropylammonium picrate was isolated from the residues of the crystallisation, as follows: the alcoholic mother-liquors were evaporated and the residue was boiled for a short time with benzene containing 5—10% of acetone, in which mixture the tetramethylammonium salt is scarcely soluble. The filtered solution yielded leaflets on cooling, which, after two crystallisations from water and two from methyl alcohol, gave stout, yellow crystals, m. p. 195—196°, consisting of pure *trimethyl*-n-*propylammonium picrate* (Found: C, 43·5; H, 5·6; N, 16·7%). This salt is much paler in colour than the tetramethylammonium salt and the progress of the separation can to some extent be followed visually. In another experiment, 6% of pure *dimethyl*-n-*propylamine*, b. p. 65—66°, was isolated by distillation of the mixed tertiary bases first over barium oxide and then over sodium (identified as picrate).

(VIII). *Trimethyl*-n-*butylammonium Hydroxide.*—These experiments were carried out in precisely the same way as those described in Section VII. We isolated 12—14% of methyl *p*-nitrobenzoate and, taking precautions to avoid loss (above), 75% (corr.) of almost pure αβ-dibromobutane, b. p. 160—165°. The carbon content of the mixed picrates (yield 93%) obtained by treating the basic product with trinitroanisole indicated the presence of 23% of trimethyl-*n*-butylammonium picrate, *i.e.*, 21 molecules %, in fair agreement with the estimate based on the yield of dibromobutane.

These results differ considerably from those of von Braun (*loc. cit.*), who claims to have obtained 50% of dried and fully rectified dimethyl-*n*-butylamine, b. p. 96°. Working on the same scale (31 g. of trimethyl-*n*-butylammonium iodide) and dehydrating the mixed bases with potash and with metallic sodium as he recommends, we obtained only 1·65 g., *i.e.*, 13%, of almost pure butyl base, b. p. 93—96°. It is difficult to avoid losses in the isolation of this substance when working on so small a scale, but it is evident from the data recorded above that von Braun's yield is much too high.

(IX). *Trimethyl-*sec.*-butylammonium Hydroxide.*—*sec.*-Butylamine was methylated with excess of methyl iodide in moist ether to which successive quantities of silver oxide were added. After addition of water and filtration, the aqueous layer was extracted with ether, titrated, and distilled. The yield of αβ-dibromobutane was about 65%, and the basic fraction consisted very largely of trimethylamine and did not contain an isolable quantity of dimethyl-*sec.*-butylamine. A portion of the liquid obtained on distilling the dilute hydrochloric acid solution in which the basic decomposition products had been collected was turbid and had the odour of *sec.*-butyl alcohol, and the methyl *p*-nitrobenzoate, obtained in very small amount from the early fractions of the distillate, was sticky, probably owing to the presence of the butyl ester. On account of the limited quantity we were able only to drain the crude methyl ester and crystallise it once, but the m. p. (88—91°) of the specimen so obtained was raised by admixture with pure methyl *p*-nitrobenzoate.

(X). *Trimethyl*iso*butylammonium Hydroxide.*—These experiments were carried out like those described in Sections VII and VIII, but a slight complication arose owing to the fact that, when the evolved *iso*butylene was passed into ice-cooled bromine, not only addition, but also a little substitution occurred with the production of hydrogen bromide. Therefore, on distilling the bromide, in addition to a considerable quantity (usually about 50%) of almost pure αβ-dibromo*iso*butane, b. p. 147—153° (Found: C, 22·4; H, 3·9. Calc.: C, 22·2; H, 3·7%), a less volatile portion was obtained having a higher proportion of bromine and lower proportions of carbon and hydrogen than correspond with the formula $C_4H_8Br_2$. This was weighed (x grams) and analysed (C, p%), and the corresponding weight of *iso*butylene taken as 0·0117 px. The mean of three concordant estimates of the total quantity of *iso*butylene produced was 63%. Methyl alcohol was qualitatively identified in the usual way (17% of methyl *p*-nitrobenzoate isolated). The basic fraction consisted mainly of trimethylamine, but also contained *dimethyl*iso*butylamine* (Found: C, 71·1; H, 15·0. $C_6H_{15}N$ requires C, 71·3; H, 14·85%), 20—25% of which was isolable in a pure condition (b. p. 80—81°; distilled over sodium). *Dimethyl*iso*butylammonium picrate* separates from methyl alcohol in canary-yellow prisms, m. p. 124° (Found: C, 43·7; H, 5·7. $C_{12}H_{18}O_7N_4$ requires C, 43·7; H, 5·5%), and *trimethyl*iso*butylammonium picrate*, prepared from the tertiary base and trinitroanisole, crystallises from water in orange-yellow needles, m. p. 173—174° (Found: C, 45·5; H, 5·9. $C_{13}H_{20}O_7N_4$ requires C, 45·4; H, 5·8%).

These results differ from those recorded by Collie and Schryver (*loc. cit.*), who obtained only traces of olefin, whilst dimethyl*iso*butylamine was their sole basic product.

(XI). *Trimethyl*-tert.*-butylammonium Hydroxide.*—These experiments were carried out like those in Section IX, with comparable results, excepting that some substitution occurred in the bromine solution. Traces of methyl alcohol were detected, but the precipitated nitrobenzoic ester was oily and could not be fully purified. From the fact that on distilling the dilute hydrochloric acid solution there was an arrest at 80° we infer the probable presence of *tert.*-butyl alcohol. Methylation of the basic fraction with trinitroanisole showed that trimethylamine was the principal constituent.

(XII). *Trimethyl*-sec.*-amylammonium Hydroxide.*—The procedure and results were similar to those of the preceding section. Traces of impure methyl *p*-nitrobenzoate, m. p. 85—90°, were obtained, together with αβ-dibromopentane, b. p. 185—190°, and trimethylamine. The formation of *n*-*sec.*-amyl alcohol was observed (compare Section IX), but it was not isolated. The tertiary base was identified by conversion into tetramethylammonium picrate.

(XIII). *Trimethyl-β-ethyl-*n*-butylammonium Hydroxide.*—β-Ethyl-*n*-butylamine (ψ-hexylamine) was prepared as recommended by Freund and Hermann (*Ber.*, 1890, **23**, 192), and the fraction, b. p. 120—123° (Found: C, 71·0; H, 15·0. Calc.: C, 71·3; H, 14·85%), methylated as described in Section IX. A considerable yield (30%) of methyl *p*-nitrobenzoate was obtained. Substitution occurred in the bromine solution, as was shown by the production of hydrogen bromide, and therefore, since the quantity of material was rather limited, the mixed bromides were not distilled, but were analysed (Found: C, 28·3; H, 4·6%), and the weight of olefin was calculated from the carbon content by the formula 0·0117 *px*, giving the value 43% of the theoretical. This figure was confirmed by analysis of the mixed picrates (yield 94%) obtained by treating the basic fraction with trinitroanisole (Found: C, 45·0; H, 5·8. Calc. for tetramethylammonium picrate: C, 39·7; H, 4·6. Calc. for trimethylhexylammonium picrate: C, 48·4; H, 6·4%. Hence, proportion of tetramethylammonium picrate = 39%, *i.e.*, 43 molecules %).

(XIV). *Trimethyl*-β-n-*propyl*-n-*amylammonium Hydroxide.*—The primary base, prepared as in the preceding case *via* di-*n*-propylacetonitrile, had b. p. 163—165° (Errera, *Gazzetta*, 1896, **26**, ii, 246, gives b. p. 167° corr.). The yield of methyl *p*-nitrobenzoate was 39%. The yield of olefin determined as in the preceding experiment was 31%, and analysis of the mixed quaternary picrates indicated the presence of 29 molecules % of tetramethylammonium picrate.

(XV). *Trimethyl*-n-*propylammonium Phenoxide.*—The quaternary iodide was converted into the hydroxide, the solution of which was concentrated until it *began* to decompose. (This point is readily ascertained from the fact that the steam entering the first acid trap is not quite completely condensed, minute residual bubbles reaching the surface.) Phenol was then added (1·05 equivs.). The incipient decomposition then ceased and a further quantity of water had to be driven off, and the temperature raised, before it recommenced, indicating the greater stability of the phenoxide than the hydroxide. The solution was distilled to dryness, the anisole collecting as an oil in the first hydrochloric acid trap. It was extracted with light petroleum, washed with sodium hydroxide and distilled (yield, 65%), b. p. 153—156° (Found: C, 77·7; H, 7·5. Calc.:. C, 77·8; H, 7·4%). The bases were converted into the quaternary picrates with trinitroanisole (yield 93%), and analysis of the mixture indicated that trimethyl-*n*-propylammonium picrate and tetramethylammonium picrate were present in the proportion 3 : 1. Both picrates were isolated by crystallisation as described above. The yield of nearly pure propylene dibromide, b. p. 135—141°, was 15%.

(XVI). *Trimethyl*-n-*propylammonium Carbonate.*—The hydroxide solution was saturated with pure carbon dioxide and distilled as usual. Methyl alcohol was formed in considerable quantity and isolated as the *p*-nitrobenzoate. The yield of propylene dibromide was 26% (uncorr.). A portion of the hydrochloric acid solution was basified in presence of ether, and the picrates (m. p. 110—115°)

precipitated with ethereal picric acid. They were dissolved in hot benzene, and, a certain time having been allowed for crystallisation, the still warm solution was diluted to twice its volume and at once filtered. The residue, after three crystallisations from alcohol, yielded pure trimethylammonium picrate, m. p. 215—216°. On evaporating the benzene solution and crystallising the residue repeatedly from ethyl acetate, pure dimethyl-*n*-propylammonium picrate, m. p. 108—109°, was obtained. Another portion of the acid solution was basified under ether, and the bases were methylated with trinitroanisole (yield 92%). Tetramethylammonium picrate, m. p. 306°, was obtained by crystallisation from alcohol, and trimethyl-*n*-propylammonium picrate, m. p. 194—195°, was isolated from the mother-liquors as previously described. Analyses of the mixed tertiary and quaternary salts indicated the proportion 3 : 1, the propyl derivatives preponderating.

(XVII). *Trimethyl*-n-*propylammonium* m-*Nitrophenoxide*.—This experiment was carried out in the same way as the preceding one, except that *m*-nitrophenol was added in place of phenol. *m*-Nitroanisole, m. p. 37—38°, was obtained in 89% yield by extracting the hydrochloric acid solution with ether, washing the extract with alkali, and evaporating it. A little olefin bromide was produced, but it was not enough to distil, and the base consisted almost wholly of *dimethyl*-n-*propylamine*, 84% of which was obtained in a pure condition (b. p. 65—66°; distilled over sodium) (Found: C, 68·8; H, 15·0. $C_5H_{13}N$ requires C, 69·0; H, 14·9%).

(XVIII). *Trimethyl*-n-*propylammonium Acetate*.—The hydroxide solution was exactly neutralised with acetic acid and distilled. Very little gas passed into the bromine, and, on removing the excess of halogen, only a few drops of oil, insufficient for distillation, remained. Methyl acetate was obtained in quantity by distilling the hydrochloric acid solution and redistilling the first portion of the distillate over calcium chloride; it was identified by its odour, boiling point, and by saponification, the methyl alcohol being characterised by means of its *p*-nitrobenzoate. The picrate obtained from the basic product had m. p. 104—106°, and 2·50 g., on crystallising from ethyl acetate, gave 2·25 g. of pure dimethylpropylammonium picrate, m. p. 107—108·5°. The quaternary picrates obtained by methylating the bases with trinitroanisole had m. p. 204—206°. Several crystallisations from water lowered this m. p. to 195—196°, the m. p. of pure trimethyl-*n*-propylammonium picrate. Since admixture with tetramethylammonium picrate raises the m. p. of trimethyl-*n*-propylammonium picrate, this is the behaviour to be expected if the original mixture contained a small proportion of tetramethylammonium picrate; the colour of the mixed salts also suggested the presence of a small amount of this substance, but we were not able to isolate it. Artificial mixtures of trimethyl-*n*-propylammonium picrate and tetramethylammonium picrate containing 9—10% of the latter behaved in all respects similarly, and we have little doubt that a small proportion of tetramethylammonium picrate was contained in the product obtained from the bases formed by decomposition of trimethyl-*n*-propylammonium acetate.

(XIX). *Trimethyl-*n*-propylammonium chloride* was prepared and distilled in the same way as the acetate. The yield of propylene dibromide, b. p. 139—140°, was 10% (uncorr.). The quaternary picrates obtained from the basic decomposition products and trinitroanisole had m. p. 213—222°, and on crystallisation from 95% alcohol yielded, first, pure tetramethylammonium picrate and then a mixture. When the latter *began* to be deposited, the solution was diluted with warm alcohol and filtered. The residue obtained on evaporating the filtrate, on repeated crystallisation from water, yielded trimethyl-*n*-propylammonium picrate, m. p. 195—196°. The non-volatile residue remaining in the flask consisted of a mixture of the chlorides of trimethylamine and dimethyl-*n*-propylamine, and on methylating the liberated bases, the corresponding quaternary picrates were obtained.

(XX). *Trimethyl-*n*-propylammonium Iodide.*—The results were comparable in all respects with those recorded in the preceding paragraph, except that the yield of propylene dibromide (13%) was a little greater.

We wish to thank the Royal Society for defraying part of the cost of this investigation.

THE UNIVERSITY, LEEDS. [*Received, February 19th*, 1927.]

CXL.—*The Passivity of Metals. Part I. The Isolation of the Protective Film.*

By ULICK RICHARDSON EVANS.

THE alteration in chemical properties conferred on iron and other metals by oxidising treatment has been attributed by some investigators to a protective film of oxide, oxygen-alloy, or other material, and by others to some essential change in the metal itself, or to the removal of a supposed catalyst. Many chemists have hesitated to accept the oxide-film theory chiefly because (1) no film is usually visible, and (2) iron which has been covered with a visible film by heating is often not passive. However, recent work (Evans, *Nature*, 1926, **118**, 51) has shown that electrolytic iron exposed to air or oxygen at different temperatures undergoes absolutely no *visible* change until the oxide film reaches the thickness requisite to give the first yellow interference tint. Thinner films are quite invisible, and yet they give good protection against attack by copper nitrate—better protection, in fact, than thick visible films, which fail locally at points representing pores or cracks, causing deposition of copper on the outer surface of the oxide scale. It is noteworthy that pure iron, rendered active by abrasion, becomes passive when exposed for a few hours to dry air at the ordinary temperature.

It seems at least possible that the production of passivity upon iron by immersion in solutions of oxidising agents, or by anodic treatment in an alkaline liquid, may be due to films too thin to give interference colours. Indeed, it is clear that the greater the specific protective character of the material composing the film the less likely is the thickness to reach the visible range, since the film will hinder its own growth by excluding the oxidising agent from the metal below; only when the protective character of the material is imperfect is a visible film to be expected. This is found to be the case. Ordinary anodic treatment in sodium hydroxide solution renders iron passive, but produces no visible change; if an alternating current is superimposed on the direct current, however, attack upon the iron occurs, and colours (straw-yellow, gold, reddish-brown, and purple) appear in turn on the iron (Allmand and Barklie, *Trans. Faraday Soc.*, 1926, **22**, 34). Likewise, immersion of iron in pure potassium chromate solution causes no corrosion and produces no marked change in appearance; but if a chloride is present in the chromate solution, corrosion occurs locally, and around the points of attack bright colours (yellow, red-mauve, and blue) may be seen, similar to those obtained by heating iron in air at high temperatures (Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T). Again, specimens of zinc partly immersed in sodium chloride solution develop colours over a zone near the water line; after drying in air, this zone is found to be blackened by copper sulphate solution more quickly than the parts of the zinc displaying no visible film (Evans, *Ind. Eng. Chem.*, 1925, **17**, 366).

In such cases, the very fact that the film has become thick enough to give colours is a sign that it is imperfectly protective. An efficient protective film will nearly always be invisible as long as it is in optical contact with highly reflecting metal. It is true that sometimes a considerable deposit can be seen on metal which has been rendered passive, but the incoherent appearance of such deposits is sufficient to show that they are not protective films, although their presence is evidence that the liquid is saturated with some compound—a condition favourable for the production of a true film. The arrival and departure of such deposits do not always correspond to the arrival and departure of passivity (compare Müller, *Z. Elektrochem.*, 1924, **30**, 401; Hedges, J., 1926, 2878).

The rational method of rendering visible a film too thin to give interference tints is to separate it from the metallic basis by dissolving away the latter from underneath; films of such thicknesses are readily visible if backed by air or a medium such as water, which has no great reflectivity. Various early attempts by the author to isolate in this way a film from passive iron were unsuccessful, probably owing to the presence of a second phase (*e.g.*, cementite, Fe_3C) which could not easily be dissolved away with the metal. Through the kindness of Dr. W. H. Hatfield, who has provided a considerable quantity of electrolytic iron, this obstacle now has been removed. The material had been fused in a vacuum in a magnesia crucible before being rolled into sheets 0·12 mm. thick. Analysis showed C, 0·04; Mn, 0·025; Si, 0·010; S, 0·013; P, 0·017; Ni, 0·09%. The main impurity (nickel) would certainly be present in solid solution, and could therefore be considered harmless. Photomicrographs of the material showed a satisfactory absence of inclusions.

Before each experiment, except where otherwise stated, the iron was ground with washed emery flour, applied on unbleached linen, which had previously been boiled out with water; it was then rubbed with filter paper. In special cases, emery paper, in seven grades of coarseness, was employed, whilst in one series of experiments a carborundum disc was used to abrade the surface.

Anodic Method of removing Transparent Skin from Passive Iron.—Specimens of iron rendered passive by immersion in a solution of potassium chromate, potassium nitrite, or sodium hydroxide, or by exposure to dry air, were subjected to anodic treatment, so as to dissolve away the metallic iron from the interior and leave the skin. This result could be obtained under a fairly wide range of conditions. In a typical experiment, a strip of iron 0·5 cm. wide was immersed in *M*/20-potassium chromate solution for 2½ hours at 22°, and was then washed and dried; the bottom of the strip was trimmed off, and the specimen was then clamped vertically in *N*/10-sodium chloride solution, so that only the lowest 1 cm. was actually immersed, and subjected to anodic treatment with a current of 6 milliamps.; precautions were taken that the cathodically-produced alkali did not come near the anode. Dissolution of the metal started at the bottom, and worked upwards; the action did not cease at the water level, for after about 16 hours the metal just above the water line was quite transparent, the whole specimen retaining essentially its original shape; however, when the transparent zone had spread upwards a few mm. above the water level, the lower portion usually broke off just above the water level, thus stopping the flow of current. Similar results were obtained with iron rendered passive by the other methods mentioned above.

After each experiment, an examination under a binocular microscope was carried out. The envelope of the electrode after anodic treatment consisted of two thin transparent parallel membranes united at the two edges. Between them was enclosed an appreciable quantity of liquid rich in ferrous chloride; a little residual metallic iron was found within the envelope in many specimens, but by far the greater part of the metal had in every case been dissolved away. The enveloping membrane consisted of ferric oxide and, probably owing to its thinness, was only pale yellowish-grey by transmitted light when freed from adhering material; but in nearly every case there was attached to it a quantity of "rusty" ferric hydroxide having a distinct yellowish-brown colour. On the immersed portion, this rusty hydroxide was often observed hanging from the outside in loose tufts, but it also occurred in the interior, where it was unequally distributed in patches clinging rather closely to the inner surfaces of the two membranes. Above the water line there was usually a much smaller amount of the yellowish-brown hydroxide, and for that reason most of the specimens became more completely transparent above the water level than below it. There was also more residual iron in the part below the water line, thus causing local opacity.

There seems but little doubt that the transparent envelope represents a skin present upon the metal before the anodic treatment commenced; the two parallel membranes represent the two surfaces of the original electrode. The envelope preserved in detail the original outline of the specimen; in some cases, the microscope revealed in the transparent skin tiny opaque inclusions arrayed along a series of parallel lines at right angles, unmistakably representing the original grinding directions; these lines are discussed later.

The yellowish "rusty" ferric hydroxide can be regarded as a hydrolysis product of ferric chloride or as an oxidation product of ferrous chloride. A reason for the fact that it occurs more frequently below the water level than above it is suggested by the ordinary principles of probability: above the water line, capillary forces will tend to keep the two parallel membranes close together, and the volume of iron salt solution enclosed between them will be small; below the water line, slight separation of the two skins may occur, and this fact (along with the possible occurrence of soluble iron salts outside the membrane) accounts for the close packing of the "rusty" patches. In only 3 experiments out of 57 was the *immersed* portion of the electrode converted into a transparent pseudomorph free from the rusty type of hydroxide; but in several cases where the central parts of the immersed portion were rendered almost opaque in places with rusty patches, the edges (where the two membranes necessarily approached close together) were seen to be transparent and nearly colourless.

It was remarkable that the transparent envelope was usually strong enough to retain the shape of the original electrode. The bulging referred to above was usually so slight as almost to escape notice; sometimes, however, the two membranes gaped far apart, with considerable distortion of the whole shape. Occasionally there was a tendency to curl up, whilst not infrequently small local rents occurred on one or both skins. Such imperfections were actually rather useful in revealing the fact that without doubt the transparent skeleton consisted of two separate membranes.

Iodine Method of Removing the Skin.—More definite information regarding the function of the skin in protecting iron was obtained by studying the action of iodine on passive iron; a saturated solution in 10% potassium iodide was found convenient. Pieces of iron were rendered passive in potassium chromate, and a deep scratch was made along the middle of each of them. They were then clamped vertically so as to be partly immersed in the iodine solution. After 2 days, the metal had become corroded through completely at numerous points along the line of the scratch, and usually also at points on the water line. Elsewhere there was no serious loss of thickness, except at isolated points mostly situated near the edges. The greater part of the surface, however, was covered with a transparent film which could easily be removed; below the skin, the metal was distinctly corroded, especially close to the scratch. One specimen removed in the early stages had areas over which the skin, although already visible, was still adherent; around the boundaries of these areas, the corrosion below the skin was very slight. This seemed to show that the detachment of the transparent skin was mainly due to the dissolution of the metal below. No evidence was obtained for the conversion of the metal itself to an inert form as suggested by Russell (*Nature*, 1925, **115**, 455; 1926, **117**, 47). The relative immunity of the unscratched places appears undoubtedly to be due to the fact that the skin obstructs the flow of iodine to them; it may be that a slow passage of iodine can occur through the film itself, but the attack takes place far more rapidly where the film has been removed, loosened, or undermined, or where cracks exist in it.

Pieces of freshly abraded iron clamped vertically in the iodine solution behaved quite differently, being corroded away completely up to the water line within a day; just above the water line, there remained a transparent zone consisting of a double membrane, evidently caused by the iodine solution rising by capillarity and corroding the metal between the two oxide skins produced by the action of the air.

The transparent skin freshly removed from passive iron after iodine treatment consisted of flakes of appreciable size, curling rolls 2 to 3 mm. long being quite common; these always broke up into microscopic fragments when washed. The flake-fragments were washed repeatedly by decantation until soluble iron salts were removed, and then examined under the binocular microscope. More than 100 different preparations of flakes, derived from iron rendered passive under different conditions, were studied, but the following features were characteristic of practically all.

The flakes consisted of non-magnetic ferric oxide, and were quite transparent; they often showed a tendency to curl into rolls. Each flake when viewed by transmitted light was seen to be covered with a series of dark lines, the nature of which depended on the preliminary abrasion of the iron. If the iron had been ground in one direction only, there was a single series of parallel dark lines on the flakes; if it had been ground in two directions, the flakes displayed two sets of dark lines intersecting at a corresponding angle. When the flakes were viewed by reflected light at a suitable angle, the dark lines were found suddenly to become bright lines, and there is no doubt that they represent the crenulations left on the surface of the iron by abrasion. Thus the film actually represents the oxidised surface of the original specimen of metal. In most preparations, series of opaque particles were also visible, arranged in rows parallel to the dark lines; these were partly residual iron and partly included grains of abrasive. The film showed a marked tendency to break up along lines parallel to the grinding directions, so that the film obtained from iron ground in two directions at right angles tended to produce roughly square or rectangular flake-fragments.

Although the flakes just described represent, beyond all doubt, the original oxidised surface of the metal, they usually carried a certain amount of secondary ferric hydroxide (doubtless due to hydrolysis of ferric iodide) which could be removed by washing with $N/10$-hydrochloric acid. Experiments performed under the microscope with acid containing thiocyanate showed that most of the dissolution of the adherent hydroxide occurred within 2 minutes, but the flakes themselves remained unchanged even after many hours. Special experiments showed that the flakes were rendered only very slightly thinner after being washed with acid for 3 hours, apart from the removal of hydroxide. However, the flakes which, before washing, appeared rusty yellow to the naked eye, became, after acid-washing, almost white when viewed suspended in water; when examined under the microscope, they still had a very pale, slightly yellowish-grey colour by transmitted light. The existence of the striæ on the flakes makes it easy to distinguish them from any fragments of that membranous ferric hydroxide film which sometimes forms on the air–water interface of ferric salt solutions, as the result of hydrolysis. This membranous hydroxide sometimes reaches "interference-colour thickness," and is entirely different in appearance and properties from the striated films; a long study of the latter made it absolutely certain that these could not be the result of hydrolysis. To avoid any possible mistake, most of the flake preparations mentioned above were obtained by using stoppered vessels entirely filled with iodine solution, thus avoiding the formation of membranous hydroxide altogether. Each preparation was divided into two portions, one only being washed with acid; each portion was examined separately.

Some further information regarding the distribution of iron in the flakes was obtained by treating them with 8% hydrochloric acid containing either ferrocyanide or ferricyanide. The former reagent conferred a beautiful blue tint on the flakes, which nevertheless retained their form for some hours; the dark lines representing the emery grooves became a deeper blue than the rest. This "blueing" treatment was found useful for showing up flakes which were so thin as to cause no appreciable absorption of light. Such flakes had been recognised previously only by the fact that they carried the usual series of dark parallel lines or opaque specks which could be clearly seen, although the material of the flake itself was invisible; the application of the "blueing" method, however, rendered visible the flakes as a whole. Ferricyanide was useful in showing up the particles of residual metallic iron, which produced a deep expanding circle of blue before the main part of the flakes showed any colour at all. Thiocyanate treatment also gave interesting information, but owing to the solubility of ferric thiocyanate a special method of application was necessary. A number of flakes, suspended in a water-drop, were placed on a glass slide under the microscope; the water was sucked away with tiny pointed strips of filter-paper, leaving the flake on apparently dry glass. Actually, of course, the glass was covered with an invisible film of moisture; consequently, on placing drops of acidified thiocyanate on the glass *near*, but not in contact with, the flakes, these assumed a pink colour within a few seconds, owing to diffusion of the salt through the moisture film.

Films Produced by Exposure to Air.—Strips of electrolytic iron freshly abraded with emery-paper were held at one end and heated red-hot at the other, so as to produce a temperature gradient. This left the iron without visible change at the cold end, but in the centre the three orders of interference tints appeared, whilst at the hot end there was a region covered with comparatively thick scale. The strip was then cooled and quickly cut into sections, which were separately treated with iodine to isolate the oxide film from each. The film peeled off in big flakes which were largest where the film was thickest. These were washed with water (portions of each also with acid) and examined microscopically.

The main portion of the oxide skin, both on the " apparently unchanged " and " interference-colour " regions, consisted of transparent, non-magnetic ferric oxide, similar to that obtained from passive iron. Opaque magnetic scale began to appear as a separate layer below the transparent films about the region of second-order colours, and became very thick at the red-hot end. Confining attention to the ferric oxide film, no sharp transition of properties was noticed on passing from the " unchanged " region to the " interference-colour " region. Apart from a gradual increase of thickness and strength of the films as one passed along the strip, the same characteristics were seen throughout. All the films showed striæ representing the original emery grinding, and in the thicker films the corrugated character of the flakes was conspicuous at the edges. Moreover, except for the very thin film at the cold end, there was a well-marked tendency to break along the directions of abrasion; the very thin flakes from the cold end were much more ragged and tended to shrivel, or to cling together in flocks, making observation difficult.

Ferric oxide films are by no means so transparent as the lead oxide films separated from heat-tinted lead (Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 231), and the light-absorption produced by the thicker films was considerable. The flakes from the second- and third-order regions, although translucent, were dark brownish-grey by transmitted light. With the thinner films, the amount of light transmitted increased; the first-order flakes were brownish- or yellowish-grey, the tint being only very slightly modified by interference (the optical principles involved will be discussed elsewhere). With the films obtained from the " unchanged " region, the light-absorption diminished still further, but the flakes retained a slight yellowish-grey tinge which was still discernible at a thickness of one-quarter of that of the first " straw-yellow " film. By matching the absorption of two different flakes with points on a wedge-form light-filter, the approximate ratio of the thicknesses could be determined. For instance, it was found that when the iron had been abraded with emery paper of " 1½ grade " (Oakey), the maximum protection of the metal against the action of either copper nitrate or iodine solution was afforded with a film of thickness about 80—90% of that of the " straw-yellow tinted " metal.* Films having a smaller or greater thickness gave less protection against both reagents. The zone of fairly great resistance to iodine extended into the yellow region, but fell off rapidly in the mauve-red, whilst the iron showing the first-order blue was eaten away almost completely in a period which caused very little corrosion of the yellow-tinted metal. Such information, however, has no general significance. As will be explained below, by the use of finer grinding materials, good protection is obtained at thicknesses far below those just quoted; indeed it is not impossible that a continuous unimolecular film extending over stress-free iron would give protection (compare Vernon's results on copper, J., 1926, 2273).

The most surprising result is that the thicknesses of different flakes taken from the same area of the specimen show a considerable variation. This becomes particularly marked in the case of the films responsible for the first-order blue and subsequent tints, and a microscopic study of these has suggested the cause. Such films when freshly removed showed numerous holes, and beside these holes, or covering them, were smaller pieces of film usually attached as " flaps " to the main films. Evidently, then, these thick films have a marked tendency to crack, as suggested by earlier work (*Nature*, 1926, **118**, 51); at each crack oxygen would gain access to the exposed metal and produce a second film below. If after the iodine treatment this second film remains adherent to the first, a local thickening will be visible at the site of the crack; if it does not adhere, a separate specimen of the second film will be obtained, which will in general be thinner than the average thickness proper to the tint under consideration. Evidence of similar thickening around sites of cracks was obtained for films too thin to produce interference tints on some specimens abraded with the carborundum disc; the cracks followed the grinding directions. In general, however, the films freshly separated from the "unchanged" region did not show cracks or holes as long as they were suspended in water, although holes developed when they were dried. The very thin flakes, which have a ragged—as opposed to a square—outline, probably represent fragments of a discontinuous film which did not completely cover the surface of the metal. It is easy to understand why the continuous films of intermediate thickness give better protection than films of greater or smaller thickness.

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* The *actual* thicknesses of the " heat-tint " films have long been the subject of discussion. If we adopt the value 2·36 for the refractive index of ferric oxide towards blue light (Kundt, *Wied. Ann.*, 1888, **34**, 484), and if we neglect the error due to the difference between the phase-changes connected with the reflexions at the two interfaces (see Evans, *J. Soc. Chem. Ind.*, 1926, **45**, 211), then the thickness of the first straw-yellow film should be about 400 Å. The thickness cannot be expressed directly in terms of layers of molecules, as this will depend on the crystal-orientation; but it may be stated that X-ray studies by Davey (*Physical Rev.*, 1923, **21**, 716) have shown that the side of the equilateral triangle formed by the three oxygen atoms of the Fe_2O_3 molecule is 5·035 Å.

We have now to consider the cause of the cracks in the thicker films, and of the discontinuity in the thinner films. The cracking in the *thick* film is undoubtedly due to the compressional stresses resulting from the fact that iron oxide occupies a larger volume than the iron required to produce it (compare Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529). The "saucer-shaped" form of scale-fragments sometimes thrown off from heated metals, especially copper, is a visible proof of this compression. Mechanical considerations show that this cracking will occur more readily with thick films than with thin.

The discontinuity of films of thickness *below* that needed to produce maximum air-passivity seems to be due to quite different causes. At first, it might be thought that it is the consequence of a limited velocity of oxidation, but experiments on film formation in air at the ordinary temperature do not support this view. Several specimens of iron were quickly ground with the carborundum disc, held in air for a definite time, and plunged into iodine. Blank experiments were made with specimens ground under the surface of iodine; these produced no flakes, except for a very small quantity which probably came from the edges of the specimens—places difficult to grind satisfactorily under these conditions. But exposure to air even for so short a time as 8 secs. produced a large crop of flakes which, although ragged and shrivelled, must have occupied a considerable fraction of the whole surface. Exposure to air for longer periods (11, 22, 43, 165 secs.; 5, 10, 20 mins.) gave flakes which became less ragged as the exposure increased. It would appear that the surface oxidation of iron at low temperatures is quite rapid, and the non-protective character of the films in the early stages is due to some other cause.

A further series of experiments showed that the time required to produce effective air-passivity to copper nitrate solution increased with the coarseness of the abrasive used to prepare the surface. Strips of iron were ground with emery paper of six different grades, and at definite intervals drops of $M/20$-copper nitrate solution were placed on them. The finest-ground strip became unaffected by the copper salt within a few minutes; that ground with the coarsest paper required some hours. No definite "periods of passivation" can be stated, since, during the transition from the active to the passive state, copper-deposition becomes confined to a limited number of points (evidently gaps in the film), and these points gradually become more and more sparsely distributed as the time goes on. During the transition period, therefore, some of the drops on a strip will show copper deposition and others none; a similar lack of reproducibility has been noticed by McCulloch (*Trans. Amer. Electrochem. Soc.*, 1926, **50**, 197), who has found that large pieces of "passive" iron are more liable to fail than small pieces, no doubt because there is a greater probability of a discontinuity occurring somewhere in the film when a large portion is being tested.

The important effect of the abrasive on the time needed for passivity suggests that the cause of local failure of the films produced by air in the early stages of oxidation is due to the internal stresses left by the grinding. A cold-worked metal is necessarily subjected, in different parts, to tensile and compressional stresses; normally the tensile stresses are in equilibrium with the compressional stresses, but if the outer surface undergoes removal or chemical alteration, this equilibrium is destroyed, as shown by Heyn (*J. Inst. Metals*, 1914, **12**, 3) and by Hatfield and Thirkell (*ibid.*, 1919, **22**, 67). When, therefore, the surface layers of cold-ground iron become converted into oxide, forces will at once become available to produce cracking in the films first formed, and although fresh oxidation will keep "repairing" the cracks, cracking will continue until the internal stresses are sufficiently diminished. This will occur quickly if the iron has been ground with fine abrasive, but will require a long time if it has been ground with coarse abrasive, thus explaining completely the observed facts.

It seems possible that the thickening of the film with time may be due rather to the passage of oxygen through the continually opening cracks than to diffusion through the substance of the film itself, diffusion through a solid being a slow process at the ordinary temperature; this would provide an explanation of the variation of the film thickness from place to place. If this explanation is correct, we may expect to find that coarse-ground iron develops films of a greater thickness than fine-ground iron. An actual study of the films from iron ground with six grades of emery confirms this expectation in a noteworthy manner, the films coming from the iron ground with the finest emery having at the most only one-quarter of the thickness of those derived from iron ground with the coarsest emery, and probably very much less. Measurement of the thinnest films is very difficult, as they contain much opaque residual iron, and the film (which seems almost incapable of existing without support) tends to shrivel around the places where this stronger supporting material is present.

When drops of $M/20$-copper nitrate are placed on specimens of iron which have previously been exposed to air for sufficient time to acquire passivity, no copper is deposited, but a sequence of interference tints slowly appears, indicating a film-thickening. This is another example of the general principle that agencies which tend to cause a film to break down may, under less favourable conditions, simply cause it to thicken. The sequence of colours indicates that the film reaches its greatest thickness at the drop-edges (the usual seat of a breakdown), and becomes continually thinner as the centre of the drop is approached; this is confirmed by converting the film, which consists of ferric oxide, *in situ* into Prussian-blue. A greater final thickness is reached, *ceteris paribus*, on coarse-ground iron than on fine-ground iron, no doubt because the initial thickness is greater when a coarse abrasive has been used.

Films produced by Potassium Chromate.—When electrolytic iron is ground in air and then placed in a solution of potassium chromate, there will usually be the beginnings of an oxide film on the metal before immersion, as a result of oxidation during grinding. As a rule, however, the metal will not be passive towards copper nitrate when it enters the solution, but it gradually acquires passivity through the action of the chromate.

Pieces of electrolytic iron were ground with emery, and at once placed in potassium chromate solution in a thermostat for definite times. The films were then removed with iodine, and studied. A " blank " was performed with metal which had been ground in air like the others, but not immersed in chromate. The flakes from the " blank " (due simply to air exposure during grinding at a temperature unavoidably raised slightly through friction) were of the ragged, shrivelling type characteristic of a discontinuous film, but gradual lengthening of the chromate treatment rendered the flakes less ragged and squarer. The aspect of the metal left after the flakes had been removed by iodine also suggested that the film became more nearly continuous with the immersion in chromate. In the blank, the metal was completely corroded away by the iodine over a large area, but as the chromate exposure was increased the area suffering perforation gradually lessened.

The main function of the chromate, in the case of electrolytic iron, is clearly to repair the discontinuities in the oxide film which had already commenced to grow during the grinding in air, but in addition there is some evidence that the chromate causes thickening of the film. Preparations of flakes were obtained from iron which had been ground with fine emery flour and immersed in *M*-potassium chromate for 4, 8, 16, 32, 128, and 256 mins., respectively, at 11·4°, and the thickness of the flakes was measured; a similar study was made of flakes separated from iron ground with coarse emery. The films obtained from every specimen showed the usual variation of thickness, the thickest flakes being generally 1½—2 times as thick as the thinnest. But there seemed little doubt that the average thickness of "typical" flakes increased somewhat with the time of exposure to chromate solution; the thickening, however, became too slow to be followed when the thickness of typical flakes reached a value about 85—90% of that obtained from iron heat-tinted to the commencement of the first-order yellow; at this stage, the film still contained thinner places (70% of the thickness of the incipient yellow) whilst individual flakes already showed a thickness which, if continuous over the whole surface, would have produced a visible yellow colour. It is not surprising, therefore, that a prolonged exposure to chromate solution can actually confer a yellow tint. Two years ago, the author (*J. Soc. Chem. Ind.*, 1925, **44**, 163T) showed that samples of commercial iron placed in potassium chromate solution for 3 weeks acquired a slight, permanent, yellow tint, whilst similar specimens placed in chromate–chloride mixtures developed yellow, mauve-red, and blue patches around the points of breakdown; the colour sequence indicated a gradual thickening of the film as the site of corrosion was approached, a phenomenon exactly analogous to the variation of thickness recognised at a lower range in the present research. Exposure to air for similar periods did not cause tinting.

Attention must be directed to one difference in the behaviour of continuous and discontinuous films. When a piece of iron, rendered passive by long immersion in potassium chromate solution, is placed in iodine for a sufficient time to loosen the skin, the specimen can be withdrawn with the film still clinging to the metal, although a layer of liquid is present between the film and metal. On gently agitating the specimen with clean water, the film comes off in quite large flakes. If, however, a freshly ground piece of iron is placed in iodine, no film is found on the metal when it is withdrawn, for any rudiments of a film produced by air-treatment during grinding have already passed away into the iodine solution, whence they can afterwards be recovered by the usual settling process.

Electrolytic iron is rendered passive by dry air as readily as by potassium chromate solution. Thus, two specimens of electrolytic iron were treated, one in dry air and the other in *M*-potassium chromate solution, for 22 hours; they were then both quite passive towards *M*/20-copper nitrate and remained quite unaffected in that solution for 13 days; even after 8 weeks, they were both bright and free from copper, although there was a little flocculating rust at the bottom of the vessels. Steel (C, 0·18; Mn, 0·56; Si, 0·04; S, 0·047; P, 0·028; Ni, 0·10%) behaved differently, however: a sample exposed as above to air broke down in *M*/20-copper nitrate within 4 minutes, copper being deposited freely; a sample treated in chromate survived for 20 minutes. Here one must consider the effect of couples set up between the iron (as anode) and cementite (as cathode); electrochemical action of the chromate will necessarily tend to build an oxide film over the anodic area, which must continue until the whole surface becomes equipotential and current ceases to flow; in that condition, the surface is likely to be equipotential in copper nitrate also. There is no *a priori* reason to suppose that exposure to dry air should bring about a surface which would be equipotential in copper nitrate solution. Hence the advantage of obtaining passivity with an electrolyte, such as potassium chromate, is obvious.

Effect of Chlorides on Passive Iron.—The well-known action of chlorides in dispelling passivity is capable of two different explanations: (1) Mere immersion in chlorides may be supposed to loosen or peptise the film, quite independently of the passage of electric current; (2) when passive iron is made an anode, the discharged chlorine ions may be capable of passing through the protective skin, producing corrosion of the metal below and so rendering the skin loose and non-protective. If the first explanation is correct, mere immersion in a chloride solution—under conditions which would preclude the existence of an *E.M.F.* between different parts of the metal—should render passive iron active; if the second explanation is right, the iron should remain passive.

Several experiments were performed to test this point. Discs of electrolytic iron were "whirled" in *M*/20-potassium chromate solution for periods of 30—60 min., thoroughly washed, and then "whirled" for a similar period in sodium chloride solutions (*N*, *N*/10, and *N*/20, in different experiments); for this purpose, the "eccentric whirler," designed to minimise the *E.M.F.*'s due to differential aëration, was employed (Evans, "Corrosion of Metals," 1926, p. 108). After whirling, the discs were taken out, washed, and dried. Spots of rust, apparently marking the site of pores relatively inaccessible to dissolved oxygen, were present on some discs, but in all cases there were large areas still bright and unchanged; many specimens—apparently those most free from pores—were practically free from rust spots. When drops of *M*/20-copper nitrate solution were applied to the rust-free areas, the metal was found in every case still to be passive, suggesting that the first explanation is wrong. Other experiments at 95° also pointed to the fact that mere immersion in a chloride solution without the passage of current does not dispel passivity. On the other hand, under conditions where the anodic discharge of chlorine ions is possible, chlorides render the iron capable of attack. Iron discs, after the whirling in potassium chromate, suffered rapid attack when made the anode in *N*/10-sodium chloride solution, an *E.M.F.* being applied from an external cell. Again, they were blackened within a minute by contact with *M*/20-copper chloride solution, the replacement of iron by copper being in effect equivalent to anodic attack; they also suffered rusting when drops of *N*/10-sodium chloride were placed on the surface, the *E.M.F.* in the latter case being attributable to differential aëration. These facts indicate that the second explanation represents the more important cause of the activating influence of chlorides.

A study of the anodic attack of previously passive iron in a chloride solution supports this view. Specimens of iron which had been ground with FF emery paper were whirled in *M*/20-potassium chromate, then washed, dried, and subjected (without trimming of the edges) to anodic treatment in *N*/10-sodium chloride solution. At numerous points, dark spots appeared, situated mainly at the parts least accessible to oxygen; they were, for instance, arranged along the grooves left by the grinding and were clustered more closely near the bottom of the electrode than near the water line; along the water line itself, however, there was a row of closely-arranged spots (rather smaller than the others), and grey patches also extended along the edges of the electrode. The whole appearance suggested that at certain points chlorine ions had pierced the skin, producing corrosion below it, and that the skin had been undermined and loosened around these points, the areas thus affected gradually spreading outwards until they met one another. Steel containing chromium, which shows efficient "air-passivity," behaved in an analogous manner. A "stainless steel" knife-blade anodically treated in *N*/20-potassium chloride solution was corroded away entirely around the edges. In the centre, corrosion occurred in circular spots; at many of these spots the blade became completely perforated, with marked undercutting of the surface of the surrounding steel, although between the spots in question the surface remained quite uncorroded.

One question still remains unanswered: Do the chlorine ions themselves perforate the skin, or do they pass through holes which already exist in the skin but which are impervious to other ions? By reason of size alone, chlorine ions might be expected to pass through pores impermeable to polyatomic ions, although our knowledge of osmotic phenomena shows that size is by no means the only factor which influences selective permeability. There is at present no convincing evidence of penetration through pre-existing pores, but the author is disposed to believe that such pores do play a considerable part in the breakdown.

Water-line Attack on Passive Metal.—Many earlier investigators have noted that a passive anode often suffers a slow dissolution, although only a small fraction of the current passing is concerned in corrosion, the remainder being devoted to the production of oxygen. In the present experiments, it was observed that this slow dissolution is mainly due to attack along the water line. A strip of electrolytic iron, 0·8 mm. broad, was subjected to anodic treatment in *N*-potassium sulphate; the cathode was a large iron plate, and the two electrodes were joined to a 6-volt accumulator before immersion in the liquid. The anode was introduced to a depth of only 3 mm., producing instantaneously a high local current density, so as to cause immediate passivity. A vigorous evolution of oxygen was observed over the immersed surface; along the water line, however, the metal was quickly eaten away, leading to perforation; after 37 mins., complete severance occurred at this level, and the lower part of the electrode—still almost uncorroded—fell to the bottom of the vessel. Several other experiments gave similar results.

With air-passive materials, anodic attack at the water line was sometimes very marked. A plate of "staybrite" steel (containing Cr, 18; Ni, 8%) was made the anode in *N*/10-sodium chloride at an average *C.D.* of about 50 milliamps./cm.^{2}. At first, it appeared to act as an inert electrode, oxygen being freely evolved, with a little chlorine. After 15 mins., however, the solution was seen to be turning yellow, and black points appeared at the water level, gradually extending to form a continuous black line. After 18 hours, the immersed portion was still practically uncorroded, but along the water level the corrosion had burrowed deep into the metal, with marked undercutting of the resistant surface layers.

Water-line attack is a marked characteristic of the passive state. The application of an external *E.M.F.* is unnecessary, for it can be produced by simple immersion in iodine solution. Previous work (*J. Soc. Chem. Ind.*, 1925, **44**, 163T) had shown that iron immersed in a chromate–chloride solution suffers intense attack along the water level, although in a chloride solution free from chromate the zone close to the water line is much *less* attacked than the part lower down; in the case of an air-passive material, the attack by a chloride solution occurs at the water line even in the absence of chromates (Stowell, Congress of Chemists, 1926). The suggestion made in previous papers—that the protective film tends at the water line to cling to the gas–liquid instead of the metal–liquid interface, thus initiating a breakdown—explains all the phenomena observed in the present research. It is not claimed that all cases of water-line corrosion are produced in this way; no doubt there are different causes for the special attack upon this region (Hedges, J., 1926, 831; Evans, *J. Soc. Chem. Ind.*, 1924, **43**, 127T; 1925, **44**, 163T; J., 1925, **127**, 2484). Indeed the term "water-line corrosion" has been used to cover many distinct phenomena, some of which do not occur strictly at the water level itself, but just above or just below it.

Action of Nitric Acid on Electrolytic Iron.—Although diluted nitric acid (*e.g.*, *d* 1·2) acts rapidly on electrolytic iron, the concentrated acid (*d* 1·4) was found to have little action. The liquid became yellow along the metal surface, and a few bubbles of gas were produced, but after about 2 mins. all reaction ceased, and the metal could be kept totally immersed in the acid for hours without change. If the acid was then poured off and the specimen quickly washed, the metal was usually found to be passive towards *M*/20-copper nitrate solution, although occasionally a specimen became covered with copper rapidly, indicating that the passivity produced by nitric acid may break down spontaneously. The specimens showed no resistance to iodine solution.

When pieces of electrolytic iron were dipped below acid of *d* 1·4, then taken out and allowed to drain, after some seconds a violent reaction would start quite suddenly at some point (usually at the top of the wetted area), and travel downwards rapidly until the whole area was evolving bubbles. Soon the reaction would die away, since the acid adhering to the strip became exhausted, and if the strip was then dipped again in acid, and moved about, the brown corrosion-product quickly dissolved away, revealing the bright metallic surface, which appeared quiescent. The spontaneous breakdown of the passivity on removing the metal from the liquid is easily understood, since drainage must soon bring the air–liquid interface close to the metal–liquid interface. The rapid transmission of the reaction downwards from the point of breakdown is perhaps partly due to an undermining of a protective film, but is probably largely connected with the fact that one of the products of the action, *viz.*, water, is known to stimulate the attack. Any reaction in which gaseous oxides of nitrogen are expelled must increase the ratio $H_2O : N_2O_5$ in the residual liquid, and thus will increase the velocity of the change. Perhaps the rise of temperature, and the passage of electric currents between the active and the passive regions as suggested by Heathcote (*J. Soc. Chem. Ind.*, 1907, **26**, 899) and Lillie (*J. Gen. Physiol.*, 1920, **5**, 107, 129), may also aid the transmission. Numerous observations support the view that one of the corrosion products is, in effect, a catalyst. When a strip wetted with nitric acid was allowed to drain until reaction had just started at a point, and was then plunged into nitric acid with sufficient motion to dissipate the corrosion products in the acid, the transmission ceased and the whole became quiescent; if, on the other hand, the reacting strip was introduced gently into the acid, so that corrosion products could accumulate, the reaction became violent at the water level, causing the strip to be eaten right through, and the lower part, which was usually quiescent, would fall to the bottom of the vessel within a minute. Heathcote's observation, that activity spreads downwards more easily than it spreads upwards, also receives an explanation if we assume that the heavy mixture of corrosion products contains a catalyst.

Of the other products of reaction, nitric oxide, nitrogen peroxide, nitrous acid, and ferric nitrate do not appear to have any marked effect in initiating attack. Nitric acid (*d* 1·4), to which either solid potassium nitrite or ferric nitrate has been added, does not act on electrolytic iron introduced into it. Indeed, ferric nitrate, the final reaction product, has been stated by Ramann (*Ber.*, 1881, **14**, 1430) to favour passivity, and this may be the explanation of the fact that intermediate concentrations of nitric acid can produce either corrosion or passivity according to the procedure employed. For instance, nitric acid (*d* 1·32) caused rapid evolution of gases when an iron strip was introduced into it, but if the strip was at once taken out of the acid and, after the evolution of gas had ceased, was then replaced, the whole remained quiescent, the ferric nitrate having produced passivity. Premature replacement of the strip while still reacting led to rapid attack, causing complete severance at the water level.

The ineffective character of the passivity produced by nitric acid renders the investigation of the protective film by the iodine method difficult, but the general analogy between the passivity produced by this and other methods suggests that nitric acid gives rise to a film which tends to break down spontaneously. It is often stated that no oxide of iron exists possessing the requisite properties. Heathcote's work on the rate of dissolution of *powdered* iron oxides by nitric acid rather supports that view. It seemed, however, advisable to perform experiments on the oxide as a *film*, rather than as a powder. Accordingly, strips of electrolytic iron were heated at one end so as to give the usual zones of interference colours due to oxide films, the unheated end remaining untinted. When they were placed in nitric acid (*d* 1·4) no change was observed in the colours even after 3½ hours at 23°; had the acid possessed a rapid solvent action on the oxide responsible for the colours, the tints would have disappeared, or at least altered, in the manner produced in a few seconds by cathodic treatment in dilute hydrochloric acid (compare Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 228). When the experiment was repeated with acid of *d* 1·2, the iron was violently attacked at the untinted end; after this end had been completely eaten away, the acid commenced to corrode the iron below the film *at the tinted end, causing it to peel off in ragged, microscopic flakes*, similar to those produced by the iodine method; the flakes remained undissolved after all the metal had disappeared. A similar peeling could be produced by concentrated acid when 6 days were allowed; in this case, there was practically no formation of bubbles, and the film was obtained in relatively large, transparent flakes. Evidently it is untrue to say that no oxide of iron is capable of resisting the acid to the required extent.

There are many indications that the action of nitric acid is actually capable of producing a film on the metal. In many of the experiments on the action of diluted nitric acid on iron, it was noticed that where the red fumes produced in the reaction swept up over the surface of the iron above the water level, the usual sequence of tints (yellow, reddish-mauve, blue, etc.) was produced, indicating the presence of a film. The very fact that the film had reached visible thickness showed that the physical character was unsuitable to give protection, and it was not surprising to find that in every case the tinted area was not passive towards copper nitrate. But it seems reasonable to suppose that under slightly different conditions the film would be more continuous and would afford better protection, whilst not reaching the thickness sufficient to produce tints; such conditions probably exist in concentrated nitric acid.

The view has sometimes been expressed that the resistance of commercial iron to nitric acid may be due partly to a film of silica, and it was anticipated that iron with a moderate content of silicon would be rendered passive with especial ease. Experiments on several types of the silicon–iron used in electrical machinery showed, however, that the alloys were not specially resistant to nitric acid; one alloy with 3·5% silicon was completely dissolved by nitric acid (*d* 1·40) under conditions which produced a quiescent state on pure iron. These silicon alloys were kindly provided by the General Electric Company.

Examination of Other Metals.—Aluminium, which had been exposed for $6\frac{1}{2}$ hours to air in a desiccator after grinding, on anodic treatment in *N*/10-sodium chloride left a skeleton containing much opaque residual metal, but also a transparent film, the structure bearing signs of the original grinding; the transparent skin was entirely different from the precipitated hydroxide formed in a different part of the cell (where the cathodic sodium hydroxide met the anodic aluminium chloride) and was clearly residual. The iodine method gave confirmation of these results. Aluminium, when freshly abraded or rendered active by immersion in *N*-sodium hydroxide, was quickly attacked by iodine; after 70 minutes' immersion in *M*/20-potassium chromate, it reacted only very slowly. Undermining of the surface layers gave transparent flakes of oxide containing opaque areas due to residual metal. It should be mentioned that the normally invisible skin present on aluminium which has been heated at 800° had already been isolated by Seligman and Williams (*J. Inst. Metals*, 1920, **23**, 169), whilst Bengough and Sutton (private communication) have lately obtained a transparent scale from aluminium previously subjected to anodic treatment in chromic acid.

Copper, when immersed in a chromate solution, becomes covered with a film thick enough to cause a visible browning; it is not surprising to find that this film causes only a temporary protection against silver nitrate. Strips of copper which had been immersed in *M*/20-potassium chromate solution yielded on anodic treatment a skeleton containing some flakes of transparent cupric oxide, bluish-grey by reflected light, some of which bore traces of the original emery treatment, or were continuous with the surface of flakes of residual metallic copper which themselves bore marks of the grinding. There was evidence that the transparent oxide film lacked mechanical strength, and the whole observation was made difficult by the presence of a very large amount of opaque cuprous oxide, bright red by reflected light—evidently a secondary product.

Russell's electronic view of passivity (*Nature*, 1925, **115**, 455; 1926, **117**, 47) is based largely on the assumption that the phenomenon is confined to a small number of metals possessing certain common features in their sub-atomic structure; undoubtedly the metals which are believed to have the sub-atomic structure in question include those which are easily obtained at will either in the active or in the passive state. There seems, however, no reason to draw a line between such metals and those in which one state is far more stable than the other. On considering the "long" form of the Periodic Table, we see on the extreme left the alkali metals, which, having highly soluble oxides, are unlikely normally to show passivity. To the right of these we find typical "A group" metals, such as aluminium and tantalum, which for some purposes can be regarded as being almost permanently passive; the oxide film causes remarkable permanence in air in spite of the negative electrode potential. To the right of these again are metals such as iron and nickel, in which both active and passive states are fairly stable, and still further to the right we find the "B group" metals which are normally active, although in several cases (copper and zinc) a fleeting type of passivity can be brought about by treatment with chromates.

Summary and Conclusions.

Passive iron is covered with a film which is too thin to give interference tints but which can be removed and thus rendered visible by dissolving away the metal below it by anodic treatment or by means of iodine. This film is the cause of the passivity; where the film is discontinuous or contains cracks, the iron is active. Chlorides favour the activation of passive iron, because chlorine ions can pass through the skin, and at anodic areas the metal is dissolved away below the membrane, which becomes loosened; mere immersion in a chloride solution, under conditions which preclude the flow of local currents, does not necessarily cause passive iron to become active. The attack on passive iron is often localised at the water level, where the film readily becomes loosened. Nitric acid is an untrustworthy reagent for producing passivity on iron, but the phenomena produced by it are probably to be ascribed to film formation, although in this case a film has not actually been isolated. Passive copper and aluminium are covered with transparent films, which have been obtained in flakes; the behaviour of these metals is in many ways analogous to that of iron, although in copper the passivity is less persistent than in iron, whilst in aluminium it is more persistent.

[*Received, August* 9*th*, 1926.
Amplified, February 27*th*, 1927.]

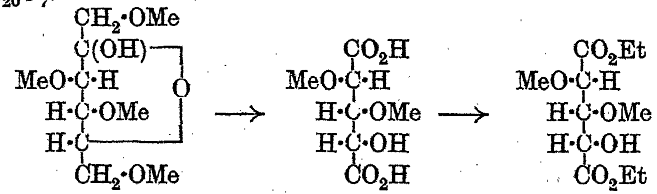
CXLI.—*The Structure of Normal Fructose: Crystalline Tetramethyl β-Methylfructoside and Crystalline Tetramethyl Fructose* (1 : 3 : 4 : 5).

By Walter Norman Haworth, Edmund Langley Hirst, and Abraham Learner.

The stable crystalline variety of tetramethyl fructose originally prepared by Purdie and Paul (J., 1907, **91**, 289) has been the subject of a constitutional study by Irvine and Patterson (J., 1922, **121**, 2696), who reached the conclusion that the structural formula of this substance was to be represented as 1 : 3 : 4 : 6-tetramethyl fructose (I). Since it is now recognised that this methylated fructose is structurally similar to ordinary fructose or lævulose, the importance of the allocation of a final constitutional formula to this sugar is evident.

Our reason for instituting an inquiry into the constitution of tetramethyl fructose was that the structure applied to this sugar presented an anomaly when compared with the new structural formulæ we have applied to glucose and other hexoses. The experimental basis for the older formulæ has been shown to be precarious, and an entirely new and fundamental investigation has been necessary in order to place the chemistry of even the simple sugars on a secure basis. Until this was achieved, it was clearly premature to interpret results with any accuracy in the field of the polysaccharides. In the present paper, we have continued our earlier inquiry (Haworth and Hirst, J., 1926, 1858) and have deemed it advisable to scrutinise closely the experimental evidence on which Irvine and Patterson based their conclusions, which have been held to support the butylene oxide formula for fructose, and for stable tetramethyl fructose (I).

These authors reported that in deciding between various competing formulæ which may represent the stable tetramethyl fructose, "the crucial reaction is the formation of dimethoxyhydroxyglutaric acid (II) by the agency of nitric acid." "This oxidation involves the conversion of the $-CH_2 \cdot OMe$ group in the 6 position into CO_2H." It was alleged that the above acid was identified by the isolation and analysis of its diethyl ester (III), which was crystalline (m. p. 86—87°), and its combustion data agreed with the calculated formula, $C_{11}H_{20}O_7$.



(I.) (II.) (III.)

We have repeated this experimental work and have isolated the crystalline oxidation product (m. p. 87—88°) described by Irvine and Patterson. The C and H analysis of this compound agrees with the molecular formula $C_{11}H_{20}O_7$, but other analytical data as well as the properties of the compound are not consistent with its identification as diethyl dimethoxyhydroxyglutarate. Thus, the titration of this substance gives results which hardly support its formulation as a dibasic ester, but are more in harmony with its recognition as a monobasic ester. It must, however, be recorded that the titration of this compound, inasmuch as it is sensitive to alkali, may easily give misleading results. When warmed with dilute alkali, it gave a yellow solution; it also reduced Fehling's solution readily. This behaviour is characteristic and points definitely to the presence of a reducing group in the substance.

We realised that the constitution of Irvine and Patterson's compound, $C_{11}H_{20}O_7$, could not be securely based on analytical evidence alone, although those authors were content to rely merely on combustion figures, remarking that the determination of methoxyl was "not diagnostic." Further study of the properties of the substance was necessary in order to furnish unmistakable reasons for the constitution (IV) which we have already proposed on other grounds (Haworth and Hirst, *loc. cit.*). The new evidence may now be briefly outlined, and it will be observed that we have relied only on crystalline derivatives which have been ultimately related to substances of definitely known structure.

The ethyl ester, $C_{11}H_{20}O_7$, m. p. 87—88° (IV), has been converted directly into the corresponding methyl ester (V), which is crystalline (m. p. 119—120°) and has the molecular formula $C_{10}H_{18}O_7$. The latter had also previously been isolated (Haworth and Hirst, *loc. cit.*) by direct treatment of the acid described by Irvine and Patterson with methyl alcohol and hydrogen chloride. From these facts it is clear that the related acid must be $C_9H_{16}O_7$, and not the dimethoxyhydroxyglutaric acid, $C_7H_{12}O_7$. This methyl ester (m. p. 119—120°), like the ethyl ester (m. p. 87—88°), reduces Fehling's solution actively, but the latter property entirely disappears on the introduction of one additional methyl group by methylation, a procedure which gives rise to a product (VI), m. p. 102°, which is stable to alkali * and is similar in the magnitude of its specific rotation to the original methyl ester, pointing to the retention of the same structural form. This product gives on treatment with methyl-alcoholic ammonia a crystalline amide (VII), m. p. 118—119°, and the nitrogen content and other analytical data

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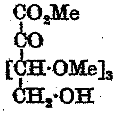
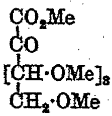
* For this reason, it seems impossible to apply to the methyl ester and the methylated methyl ester the formula of an open-chain ketone such as (A) or (B).

(A) 

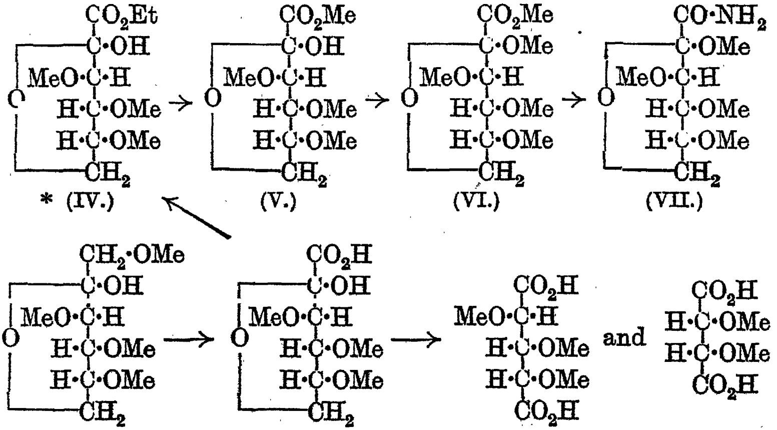
$$\begin{array}{l} CO_2Me \\ | \\ CO \\ | \\ [CH\cdot OMe]_3 \\ | \\ CH_2\cdot OH \end{array}$$

(B) 

$$\begin{array}{l} CO_2Me \\ | \\ CO \\ | \\ [CH\cdot OMe]_3 \\ | \\ CH_2\cdot OMe \end{array}$$

The cyclic formulæ (V) and (VI) which we have assigned to these products suggest their relation to the monobasic acid obtained by Ohle, Koller, and Berend (*Ber.*, 1925, **58**, 2577) by oxidation of β-fructose-diacetone with permanganate.

of this derivative point to its being the amide of a (methylated) monocarboxylic acid, $C_9H_{16}O_7$. Moreover, we have degraded Irvine and Patterson's ethyl ester (m. p. 87—88°) by further oxidation with nitric acid, and the products isolated were recognised through their crystalline amides. These were (*a*) *d*-arabo-trimethoxyglutaramide, m. p. 227°, and (*b*) inactive dimethoxysuccinamide, m. p. 246°.



* (IV.) (V.) (VI.) (VII.)

(VIII.) (IX.) (X.) and (XI.)

It is evident that *d*-arabo-trimethoxyglutaric acid (X) and *i*-dimethoxysuccinic acid (XI) could not be derived from a primary oxidation product formulated by Irvine and Patterson as in (II) or its ethyl ester as in (III), but the isolation of these acids is consistent with the allocation of the structural formula (IX), or the ethyl ester (IV). For reasons already given in the footnote, an open-chain ketonic formula for the ethyl ester is excluded, and the behaviour of the product both on methylation and on oxidation favours the adoption of the formula (IV). It may be added that the high lævorotation of the substance, which is almost identical with that of the original crystalline tetramethyl fructose, also supports the formulation as a cyclic compound, as does the persistence of the reducing group during treatment with an acid oxidising agent. Had there been present a $>CO$ linking or a terminal $-CH_2{\cdot}OH$ group, neither of these could have survived the treatment with nitric acid. In either event, the evidence from the further oxidation of this product supports our final conclusions ascribing a structure to tetramethyl fructose.

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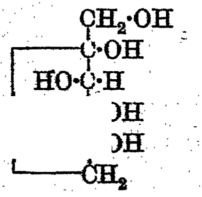
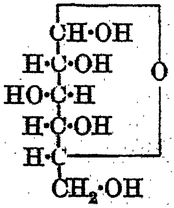
* The oxygen of the ring is not actually directed to the left as shown in these plane formulæ, but is in the same plane as the five carbon atoms of the ring; nor is it implied that the reducing group is necessarily on the right.

In the earlier paper (Haworth and Hirst, *loc. cit.*), it was observed that accompanying the acid $C_9H_{16}O_7$, which we formulate as in (IX), there was also isolated from the oxidation experiments arabo-trimethoxyglutaric acid (X) and *i*-dimethoxysuccinic acid (XI), and it is now made clear that these two acids may be regarded as secondary oxidation products formed by the breakdown of the primary oxidation product (IX) which has been isolated as its ethyl ester (IV) and its methyl ester (V). It would appear that the formation of these secondary products, which alone are of service in determining the ring structure of normal crystalline tetramethyl fructose, eluded the observation of Irvine and Patterson, since they did not examine the liquid esters which were evidently absorbed on porous tile.

The position, therefore, is that had the previous workers ascribed what we now consider to be the correct molecular formula to the primary oxidation product $C_9H_{16}O_7$ or its ethyl ester (IV), this could not in itself have resolved the difficulties attending the determination of the constitution of normal tetramethyl fructose, since the positions of the methoxyl groups would have remained undetermined and also the positions of the oxygen bridge. The cyclic structure of the original hexose appears to be still retained in this oxidation product. Such a result is as unexpected as it is remarkable in the sugar group, inasmuch as during the prolonged treatment with a drastic oxidising agent such as nitric acid (either of concentration *d* 1·2 or *d* 1·42) the first grouping to suffer attack is not the reducing group, which is preserved intact in the primary stage, but the terminal group (1), namely, the $-CH_2{\cdot}OMe$ group. The grouping in position (6) appears to be unimpaired, the allocation of the carboxyl group to position (6) being rendered impossible by the series of transformations recorded above. These observations serve to explain why normal tetramethyl fructose resists the oxidising action of bromine water and emphasise the stability of the amylene oxide ring, which must now be regarded as a constituent part of this sugar. The parallel behaviour of tetramethyl γ-fructose will be described in a subsequent paper, but here the inter-conversions which have been traced are still more remarkable and furnish an entirely novel conception of the behaviour of sugars.

(XII.)





(XIII.)

In view of the evidence now adduced, supplementing that already furnished (Haworth and Hirst, *loc. cit.*), we consider that the stable crystalline variety of tetramethyl fructose should be indexed as 1 : 3 : 4 : 5-tetramethyl fructose (VIII) containing a 2 : 6-oxide ring. Evidently, ordinary crystalline fructose contains the same structure, and is to be regarded as having also a 2 : 6- or amylene oxide ring (XII), thus bringing normal fructose into line with the revised formula for normal glucose (XIII).

It may also be added that tetramethyl β-methylfructoside, which had previously been described as a colourless liquid, $[\alpha]_D$ − 120·1° in methyl alcohol (Steele, J., 1918, **113**, 257; Irvine and Patterson, J., 1922, **121**, 2696), has now been isolated as a crystalline compound, m. p. 33—34°, $[\alpha]_D$ − 149·1° in water. An improved method of preparation leading to the isolation of this substance in a pure state has been adopted, namely, by subjecting tetra-acetyl β-methylfructoside, as isolated by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216), to the action of alkali and methyl sulphate. The replacement of acetyl groups by methyl groups is completed finally by means of Purdie's reagents.

EXPERIMENTAL.

Preparation of Tetra-acetyl Fructose.—The method of preparation described by Hudson and Brauns (*J. Amer. Chem. Soc.*, 1915, **37**, 2736) was adopted with slight modifications introduced by our colleague, Mr. C. F. Allpress. Finely powdered *d*-fructose (100 g.) was added with constant stirring to 500 c.c. of acetic anhydride, containing 9 g. of zinc chloride, maintained near 0°. After 2 hours, the temperature was kept at 10° for ½ hour, and thereafter at 16° for 2 hours. Then followed the usual treatment with water (500 c.c.), neutralisation with sodium bicarbonate, and extraction of the product with chloroform. The crystalline tetra-acetyl fructose was most conveniently isolated from the dried chloroform extract in the following way. After removal of the solvent by distillation under diminished pressure, an equal volume of ether was added to the warm syrupy residue and, on cooling, the crystalline material separated in a form which could readily be filtered and freed from adhering syrup by washing with ether. Alternatively, the sticky mass of crystals and syrup obtained by Hudson and Braun's method could be extracted with boiling ether, the syrup being thereby removed. Recrystallisation from alcohol gave the pure substance, m. p. 127—129°.

Conversion of Tetra-acetyl Fructose into Tetramethyl β-Methylfructoside.—The tetra-acetyl fructose was treated with methyl iodide and silver oxide to give in quantitative yield tetra-acetyl methylfructoside, the reagents being used in the proportions given by Irvine and Patterson (*loc. cit.*). The tetra-acetyl methylfructoside was then de-acetylated and methylated in one operation. To 30 g. of tetra-acetyl methylfructoside was added slowly at 50° with very efficient mechanical stirring the theoretical amount of 20% aqueous sodium hydroxide necessary to effect de-acetylation. This was completed in 3 hours. The temperature was then raised to 70° while 76 c.c. of methyl sulphate and 70 g. of sodium hydroxide, dissolved in 140 c.c. of water, were added during a period of 2¼ hours, the concentration of alkali being maintained throughout at about 10%. No darkening in colour took place and after extraction with chloroform in the usual way a pale yellow, mobile syrup was obtained (average yield 13 g.). This on distillation yielded 11 g., b. p. about 103°/0·14 mm., $n_D^{16°}$ 1·4578, $[\alpha]_{5780}$ − 120°; OMe, 55%. Methylation was completed by three successive treatments of the distillate with silver oxide and methyl iodide. This gave, in practically undiminished amount, tetramethyl methylfructoside in the form of a liquid, b. p. 105—106°/0·06 mm., $n_D^{16°}$ 1·4560. After being kept for a few hours, the material began to crystallise spontaneously, and on cooling in an ice-bath a solid mass of hard, flat prisms was obtained. The solid (m. p. 24°) was very soluble even in light petroleum, but by conducting all operations at 0° recrystallisation from this solvent to give pure tetramethyl β-methylfructoside was found to be possible. Four recrystallisations sufficed to raise the m. p. to 33—34°, further treatment being without effect on the m. p. (Found: C, 52·7; H, 8·8; OMe, 60·0. Calc.: C, 52·8; H, 8·8; OMe, 62·0%). The substance showed $[\alpha]_D^{17°}$ − 149·1° in water ($c = 3·1$) and behaved as a typical glucoside towards Fehling's solution; after hydrolysis with 3% aqueous hydrochloric acid at 95° for 1 hour, crystalline tetramethyl fructose was obtained in excellent yield (after recrystallisation from petroleum, m. p. 98—99°, mixed m. p. with an authentic specimen, 98—99°).

Oxidation of Normal Tetramethyl Fructose.—Crystalline tetramethyl fructose (8 g.) was oxidised with nitric acid (*d* 1·2) under the conditions described by Irvine and Patterson (*loc. cit.*). Removal of the nitric acid under diminished pressure was followed by esterification of the oxidation product in the usual manner, ethyl alcohol containing 4% of hydrogen chloride being used. After neutralisation with silver carbonate, the solution was evaporated to a syrup, which was dissolved in a mixture of chloroform and ether. Some solid matter was then filtered off, and after the rest of the solvent had been removed addition of light petroleum precipitated an oil which rapidly crystallised. After 15 hours, sufficient ether was added to dissolve adhering syrup and the crystals were separated by filtration (yield 2·3 g.). Distillation of the syrup remaining in the mother-liquor gave a fraction (bath temp. 170°/10 mm.) which crystallised on cooling to give a further amount of crystalline matter, from which the adhering syrup was removed by absorption in porous tile (total yield of the crystalline product, 3·1 g.). The complete examination of this syrup has already been described in the earlier paper by Haworth and Hirst.

Properties of the Ethyl Ester, $C_{11}H_{20}O_7$.—After recrystallisation from light petroleum the substance showed m. p. 87—88°; $[\alpha]_D$ $-98°$ ($c = 0·928$) in water. It reduced Fehling's solution strongly on warming and was unstable towards hot alkali, giving yellow solutions. For this reason, the titration figures are necessarily inexact and indicate a higher value for CO_2Et than is actually the case. Thus, 0·0917 g. required under standard conditions 4·3 c.c. of *N*/10-sodium hydroxide. This quantity of a substance of formula $C_{11}H_{20}O_7$ calculated as monobasic requires 3·5 c.c.: as dibasic (compare Irvine and Patterson) 7·0 c.c. The formulation as ester of a dibasic acid may therefore be ruled out (Found: C, 49·7; H, 7·7; OMe, 44·9. Calc.: C, 50·0; H, 7·6; OMe, 47·0%).*

Conversion of the Ethyl Ester $C_{11}H_{20}O_7$ *into the Corresponding Methyl Ester*.—The ethyl ester (0·5 g.), dissolved in 15 c.c. of methyl alcohol containing 4% of hydrogen chloride, was gently boiled for 7½ hours. The acid was then neutralised with silver carbonate, and the product isolated in the usual manner. Recrystallisation from ether yielded in all 0·33 g. of a substance identical in all respects with the methyl ester ($C_{10}H_{18}O_7$, m. p. 119°) previously isolated in the course of oxidation experiments with normal tetramethyl fructose. M. p. 119°; mixed m. p. with an authentic specimen 119° (compare Haworth and Hirst, *loc. cit.*).

Preparation of Amide from the Methylated Methyl Ester, $C_{11}H_{20}O_7$ (m. p. 102°).—Owing presumably to complication following on the action of ammonia on the reducing group, it was not found possible to isolate an amide from the methyl ester, $C_{10}H_{18}O_7$. After methylation, however, the non-reducing methylated methyl ester, $C_{11}H_{20}O_7$ (the preparation and properties of which have already been described, Haworth and Hirst, *loc. cit.*), was obtained and readily gave a crystalline amide. A solution of ester in methyl alcohol

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* The substance $C_{11}H_{20}O_7$ contains one OEt group and three OMe groups. In such a case, it is convenient for comparative purposes to calculate the OMe percentage for the figures of the Zeisel experiment in the usual way. This is then compared with the theoretical value calculated on the basis of reckoning four OMe groups per molecule of $C_{11}H_{20}O_7$.

(0·3 g. in 2·5 c.c.) was saturated with ammonia at 0° and allowed to remain at room temperature for 4 days. The ammonia and methyl alcohol were then removed under diminished pressure at 25°. The remaining thick syrup crystallised on being rubbed, but the crystals were contaminated with oil. Much of the oil was removed by recrystallisation from a mixture of benzene and petroleum (b. p. 60—80°). Final purification was effected by recrystallisation from light petroleum, needles or long, thin, flat plates being obtained, m. p. 118—119°; $[\alpha]_D$ (approximately) $-137°$ in water ($c = 0·94$) (Found: C, 48·3; H, 7·6; N, 5·5; OMe, 48·4. $C_{10}H_{19}O_6N$ requires C, 48·2; H, 7·6; N, 5·6; OMe, 49·8%).

Oxidation of the Ethyl Ester, $C_{11}H_{20}O_7$ (m. p. 87—88°).—The crystalline ester (1·68 g.) was treated with 22 c.c. of nitric acid (d 1·42) at 60°. Oxidation commenced at this temperature, and as the reaction proceeded the temperature was gradually raised to 90—95° and maintained there for 3 hours. The product was isolated as the methyl ester by the usual procedure. On removing the solvent preparatory to purification of the product by distillation under diminished pressure, partial crystallisation took place. The adhering syrup was dissolved in ether and the crystals were separated. They were found to be the methyl ester, $C_{10}H_{18}O_7$ (m. p. 119°), corresponding to the ethyl ester, $C_{11}H_{20}O_7$, used as starting material. Yield 0·53 g.; m. p. and mixed m. p. with authentic specimen 119°. This portion had therefore not undergone oxidation. The syrupy portion of the oxidation product was distilled to give 0·45 g. of colourless syrup, boiling at a bath temperature 160—165°/10 mm.; $n_D^{12°}$ 1·4446. This was dissolved in 3 c.c. of methyl alcohol saturated with ammonia. Rapid deposition of crystalline material began at 20 hours from the start of the experiment. The first crop (0·06 g.) was a mixture (m. p. about 210—215°) which was shown to contain inactive dimethoxysuccinamide by dissolving it in a slight excess of methyl alcohol, nucleating the solution with crystals of the amide in question, and allowing it to evaporate very slowly. The first crystals deposited had the characteristic shape of *i*-dimethoxysuccinamide and gave m. p. 246° (decomp.), and were identified by comparison with genuine *i*-dimethoxysuccinamide. In these comparisons of m.p.'s, it is important that the determinations should be conducted under parallel conditions. By rapid heating, the m. p. can be raised as high as 262°. After 40 hours, a crop of crystals was obtained which, after being washed on the filter with methyl alcohol and ether, proved by comparison with an authentic specimen to be arabo-trimethoxyglutaramide; m. p. 227—228° (decomp.), $[\alpha]_D$ $-48°$ in water ($c = 0·2$) (Found: OMe, 39·4. Calc.: OMe, 42·2%).

The authors express gratitude to the Department of Scientific and Industrial Research for the award of a maintenance grant to one of them (A. L.).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

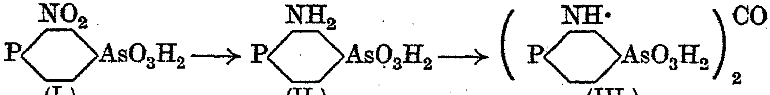
[*Received, March 28th,* 1927.]

CXLII.—*Trypanocidal Action and Chemical Constitution. Part VI. Amphoteric* s-*Carbamidoarylarsinic Acids.*

By HAROLD KING.

THE physiological action of a drug is primarily a matter of its distribution in the tissues, and among the trypanocidally active aromatic arsinic acids experience has shown that those of an amphoteric nature are the more frequent. This may be attributed to the favourable distribution conferred on substances built somewhat analogously to the simple protein units, the amino-acids. In an earlier communication (Part I; J., 1924, **125**, 2595), it was shown that the *s*-carbamides of some complex aromatic arsinic acids were devoid of trypanocidal action and it was conceivable that this was associated with their non-amphoteric nature. It was therefore deemed of sufficient interest to examine some *s*-carbamidoarsinic acids which still retained a free basic centre. These could be prepared by phosgenation of aminoarsinic acids containing a second basic centre unattacked by phosgene (carbonyl chloride) or by nitration and reduction of *s*-carbamidoarsinic acids. Instances of both classes are recorded below.

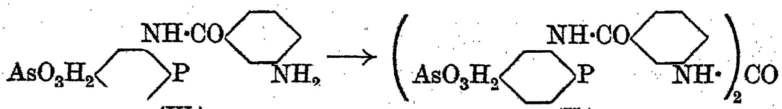
As an example of the first type, 4-chloro-3-nitrophenylarsinic acid on treatment with piperidine gave 3-*nitro*-4-*piperidinophenylarsinic acid* (I), which can be reduced to the amino-acid (II). This gives an *acetyl* derivative and also, on phosgenation, a s-*carbamide* (III).



(I.) (II.) (III.)

$$P = C_5H_{10}N.$$

On *m*-nitrobenzoylation, (II) gave 3-m-*nitrobenzamido*-4-*piperidinophenylarsinic acid*, which on reduction gave the 3-m-*aminobenzamido*-derivative (IV); and this on phosgenation gave the

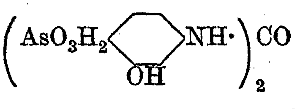


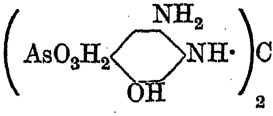
(IV.) (V.)

s-*carbamide* (V). These acids were relatively toxic to mice and had no influence on an experimental infection of *Trypanosoma equiperdum* in mice.

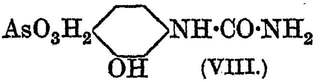
As an example of the second type, 4-amino-2-hydroxyphenylarsinic acid on phosgenation gave the s-*carbamido*-derivative (VI), which could be dinitrated to the s-*carbamide* of 5-*nitro*-4-*amino*-2-*hydroxyphenylarsinic acid.* The latter acid on reduction with sodium hyposulphite gave the 4-s-*carbamide* of 4 : 5-*diamino*-2-*hydroxyphenylarsinic acid* (VII). For comparison with the symmetrical carbamides (VI) and (VII), 2-*hydroxy*-4-*carbamidophenylarsinic acid* (VIII) was prepared by the action of potassium cyanate on 4-amino-2-hydroxyphenylarsinic acid. The maximum dose tolerated by mice expressed in milligrams per gram of mouse, and the minimum curative dose on an experimental infection of *Trypanosoma equiperdum* in mice, of these three carbamides are shown below, r signifying the number of days before relapse occurred.

(VI.)





(VII.)

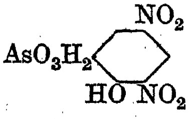


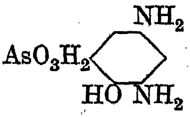
(VIII.)

	VI.	VII.	VIII.
Dosis tolerata	0·3	0·8	0·4
Dosis curativa	—	0·8	0·4
		$r = 11$ days.	$r > 30$ days.

The facile way in which the amino-group in 5-nitro-2-aminophenol can be replaced by the arsinic acid group by the Bart–Schmidt reaction (Bauer, *Ber.*, 1915, **48**, 1582; Hewitt and King, J., 1926, 817) suggested its application to picramic acid, which likewise forms an intermediate sparingly soluble quinone-diazide. Here again a good yield of the acid, 3 : 5-dinitro-2-hydroxyphenylarsinic acid (IX), was produced, probably identical with the acid obtained by Benda (*Ber.*, 1911, **44**, 3296) by the nitration of 5-nitro-2-hydroxyphenylarsinic acid.

(IX.)



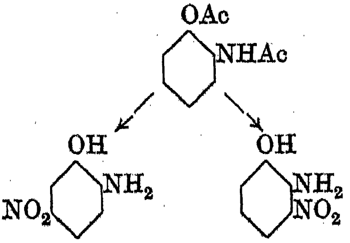


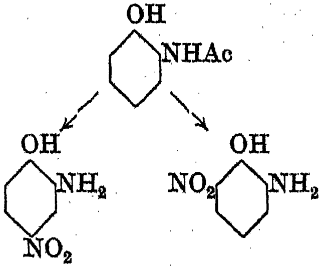
(X.)

On reduction with sodium hyposulphite it gave a new *diaminohydroxyphenylarsinic acid* (X), of which only two isomerides are known. This proved to be very toxic to mice and was devoid of trypanocidal action.

Nitration of 2- and 4-Aminophenols.

In Part IV of this series (Hewitt and King, *loc. cit.*) it was shown that *N*-acetyl-2-aminophenol or *ONN*-triacetyl-2-aminophenol, when nitrated in sulphuric acid solution with one equivalent of nitric acid, gave mainly 4 : 6-dinitro-2-aminophenol (picramic acid), but that ethenyl-2-aminophenol under similar conditions gave 5- and 4-nitro-2-aminophenols, approximately in the proportion 4 : 1. It has now been shown that *ON*-diacetyl-2-aminophenol in sulphuric acid also nitrates with production of a large proportion of picramic acid and a small proportion of 4-nitro-2-aminophenol. Meldola and Wechsler (P., 1900, **16**, 180) showed that nitration of *ON*-diacetyl-2-aminophenol by fuming nitric acid gave solely 4 : 6-dinitro-2-aminophenol, which they oriented by conversion into 2-chloro-4 : 6-dinitrophenol. This constitution has been confirmed by other means in the present communication, such confirmation being necessary since Ingold and Ingold (J., 1926, 1321), in repeating the earlier work of Meldola, Woolcott, and Wray (J., 1896, **69**, 1330), ascribed the constitution 3 : 5-dinitro-2-aminophenol to this substance, as it was deemed to be in agreement with their results on the mononitration of *ON*-diacetyl-2-aminophenol in acetic anhydride solution. The latter nitration, which leads to the formation of 3- and 5-nitro-2-aminophenols, is of considerable interest, because it has now been shown that under exactly parallel conditions *N*-acetyl-2-aminophenol gives good yields of the other two isomerides —4- and 6-nitro-2-aminophenols—and a small proportion of picramic acid.





These results, at first sight somewhat involved, bear a simple interpretation, since it has been found that *O*-acetyl is hydrolysed to hydroxyl when *ON*-diacetyl-2-aminophenol is dissolved in cold concentrated sulphuric acid and that, although *ON*-diacetyl-2-aminophenol is moderately stable in concentrated nitric acid at — 5°, when nitration has taken place the products have the hydroxyl group free, pointing to immediate nitration after hydrolysis. In either case, solution in sulphuric acid or nitric acid, if hydrolysis precedes nitration the results are consistent.

The apparent nitration of mono-, di-, or tri-acetyl-2-aminophenol in sulphuric acid or of *ON*-diacetyl-2-aminophenol in fuming nitric acid is therefore really the nitration of *N*-acetyl-2-aminophenol and in each case, whether the solvent be sulphuric acid, nitric acid, or acetic anhydride, the nitro-groups enter positions ortho or para, or ortho and para, to the hydroxyl group. When the hydrolysis of *O*-acetyl is prevented by use of acetic anhydride, the nitro-groups enter the ortho- or the para-position to the *N*-acetyl group. These results are in complete agreement with the observations of Reverdin and his associates on the nitration of *N*-acetyl-4-aminophenol (Reverdin and Dresel, *Ber.*, 1905, **38**, 1593), *ON*-diacetyl-4-aminophenol (R. and D., *Ber.*, 1904, **37**, 4453; 1905, **38**, 1593), *N*-benzoyl-4-aminophenol (Reverdin and Delétra, *Ber.*, 1906, **39**, 125), and *ON*-dibenzoyl-4-aminophenol (Reverdin and Dresel, *Ber.*, 1904, **37**, 4453; Reverdin and Delétra, *Ber.*, 1906, **39**, 125), where, however, *O*-acetyl and *O*-benzoyl are not hydrolysed prior to nitration by solution in nitric acid, but *O*-benzoyl is hydrolysed prior to nitration by solution in sulphuric acid. The relative orienting powers for nitro-groups as determined for these aminophenols may be conveniently summarised as follows :

2-Aminophenol.	*4-Aminophenol.*
OH > NHAc	OH > NHAc *or* NHBz
NHAc > OAc	NHAc > OAc; NHBz > OBz

The fact that, with the same solvent, acetic anhydride, and the same nitrating agent, nitric acid or acetylnitric acid, *N*-acetyl-2-aminophenol nitrates ortho and para to the hydroxyl group whilst *ON*-diacetyl-2-aminophenol nitrates ortho and para to the *N*-acetyl group is strong evidence in favour of the view that the induced polarity of the benzene molecule is independent of the solvent or nitrating agent as a major influence, and is probably an electromeric phase of the molecule induced by the substitution of the hydroxyl and amino-groups. From this point of view it is not difficult to understand the peculiar nitration of ethenyl-2-aminophenol which gives 5- and 4-nitro-2-aminophenols, there being two induced electromeric phases. That the solvent or nitrating agent is not without influence is shown by the great tendency for N-acetyl-2-aminophenol to become dinitrated in sulphuric acid solution, although but one equivalent of nitric acid be added, whereas in acetic anhydride solution this is a subsidiary phenomenon.

The author is deeply indebted to Miss F. M. Durham and Miss J. Marchal of this Department for the determination of the trypanocidal activities of the substances herein recorded, to Dr. J. Marshall of the Research Laboratories of Messrs. Boots Pure Drug Co. for a

gift of 4-chloro-3-nitrophenylarsinic acid, and to Dr. J. T. Conroy of the United Alkali Co. for a liberal and free supply of phosgene.

EXPERIMENTAL.

3-*Nitro*-4-*piperidinophenylarsinic Acid* (I).—4-Chloro-3-nitrophenylarsinic acid (2·81 g.) and excess of piperidine (5·4 c.c.) were boiled together in 20 c.c. of alcohol for 3 hours. The orange-coloured solution was diluted with water, evaporated to a small volume under reduced pressure, and made neutral to Congo-paper. The gum that separated in quantitative yield, and soon crystallised on being rubbed, was dissolved in 60 c.c. of 0·4*N*-ammonia, and excess of calcium chloride solution added; the finely divided *calcium* salt thus obtained was washed, suspended in water, and treated with hydrochloric acid (Congo-paper). The required *acid* (3·0 g.) separated in pale yellow leaflets (Found : As, 22·3. $C_{11}H_{15}O_5N_2As$ requires As, 22·7%). It crystallises from boiling water in laminated leaflets, is readily soluble in hot acetic or warm 90% formic acid, and dissolves in concentrated hydrochloric acid, forming an almost colourless solution. The *barium* salt separates in filmy leaflets when an ammoniacal solution of the acid is boiled with barium chloride.

3-*Amino*-4-*piperidinophenylarsinic Acid* (II).—The above-described nitro-acid (14·8 g.) was reduced with ferrous chloride and alkali in the usual manner. The filtrate from the ferric hydroxide and the weakly alkaline extracts thereof were neutralised (Congo-paper), and concentrated under reduced pressure at 50°. The crystalline *amino-acid* (10·3 g.) thus obtained was purified by solution in 50 c.c. of *N*-hydrochloric acid and careful addition of saturated sodium acetate solution till acidity to Congo-paper was removed (yield 75%) (Found : loss at 100°, 6·0. $C_{11}H_{17}O_3N_2As,H_2O$ requires H_2O, 5·7. Found in anhydrous material : As, 25·2. $C_{11}H_{17}O_3N_2As$ requires As, 25·0%). This amino-acid is instantly soluble in excess of *N*-hydrochloric acid, and yields, with nitrite, an orange-brown solution which couples intensely with alkaline β-naphthol. The pure acid readily forms, when the excess of mineral acid in *N*-hydrochloric acid solution is removed by sodium acetate, a *monohydrochloride*, which crystallises in well-formed, clear prisms (Found: Cl, 10·2. $C_{11}H_{17}O_3N_2As,HCl$ requires Cl, 10·5%). In ammoniacal solution, the acid yields a crystalline *calcium* salt, but the *magnesium* and *barium* salts are precipitated only on boiling. The maximum tolerated dose is 0·01 mg. per g. of mouse.

3-*Acetamido*-4-*piperidinophenylarsinic acid* was prepared from the foregoing amino-acid by shaking its alkaline solution with excess of acetic anhydride, added in portions. On neutralisation to Congo-paper, it separated in small prisms. The yield was quantitative (Found : As, 22·4. $C_{13}H_{19}O_4N_2As$ requires As, 21·9%). This acid is sparingly soluble in boiling water, readily soluble in boiling acetic acid, and crystallises therefrom in diamond-shaped plates. It is instantly soluble in 90% formic acid and in *N*-mineral acids. The maximum tolerated dose is 0·03 mg.

3-m-*Nitrobenzamido-4-piperidinophenylarsinic Acid.*—Amino-piperidinophenylarsinic acid monohydrate (6·0 g.), dissolved in 90 c.c. of water containing 2 mols. of sodium hydroxide, was shaken for ½ hour with 7·4 g. of *m*-nitrobenzoyl chloride, and at half-hourly intervals two further quantities of 20 c.c. of *N*-sodium hydroxide were added. On the solution being made definitely acid (Congo-paper) the required *acid* separated, as a gum which rapidly crystallised, mixed with nitrobenzoic acid. The latter was removed by ether extraction. The yield was 92%. For analysis, the acid was purified by solution in dilute aqueous alkali and very gradual precipitation of the warm solution with acid (Found : loss at 100°, 7·3. $C_{18}H_{20}O_6N_3As,2H_2O$ requires H_2O, 7·4. Found in anhydrous material : As, 17·1. $C_{18}H_{20}O_6N_3As$ requires As, 16·7%). This acid is readily soluble in boiling acetic acid and crystallises well in spiked rods. It is soluble in concentrated hydrochloric acid, but is precipitated in well-formed, flattened prisms on dilution. In ammoniacal solution, it yields crystalline precipitates of the *calcium* and *barium* salts on addition of the corresponding chlorides.

3-m-*Aminobenzamido-4-piperidinophenylarsinic Acid* (IV).—The foregoing nitro-acid (7·3 g.) was reduced with ferrous chloride and alkali, and the ferric hydroxide precipitate extracted with dilute alkali solution. The combined filtrates were neutralised (Congo-paper), a copious, amorphous precipitate separating; from the filtered solution, concentrated under reduced pressure, a crystalline acid separated. This was dissolved in *N*-hydrochloric acid and fractionally precipitated from the hot solution by saturated sodium acetate solution. After removal of much weakly basic, amorphous material, the required *amino-acid* was obtained in poor yield (2·25 g.) (Found : As, 18·2. $C_{18}H_{22}O_4N_3As$ requires As, 17·9%). This amino-acid is extremely readily soluble in *N*-hydrochloric acid and diazotises and couples with alkaline β-naphthol with formation of a red precipitate insoluble in excess of alkali. In hot ammoniacal solution, it yields a *magnesium* salt, narrow plates, and a *barium* salt, clusters of leaflets, on addition of the corresponding chlorides. The maximum tolerated dose is 0·1 mg.

s-*Carbamide* of 3-*Amino-4-piperidinophenylarsinic Acid* (III).—Into a solution of the amino-compound (3 g.) in 200 c.c. of water containing 21·2 g. of anhydrous sodium carbonate (20 mols.), carbonyl chloride was passed until an acid reaction was obtained. The crude arsinic acid was precipitated by adjusting the reaction to faint acidity to Congo-paper. It was recrystallised by solution in 30 c.c. of *N*-ammonia and addition of concentrated hydrochloric acid, separating as a microscopic, white powder (yield 2·9 g.) (Found: loss at 100°, 2·9. $C_{23}H_{32}O_7N_4As_2,H_2O$ requires H_2O, 2·8. Found in the anhydrous acid: As, 23·8. $C_{23}H_{32}O_7N_4As_2$ requires As, 23·9%). This acid is almost insoluble in boiling glacial acetic acid, but dissolves readily on addition of a small proportion of water and then crystallises, on cooling, in microscopic rods. It is readily soluble in 3*N*-hydrochloric acid. The *magnesium* salt crystallises in elongated leaflets from ammoniacal solution containing ammonium chloride. The maximum tolerated dose is 0·075 mg.

s-*Carbamide of* 3-m-*Aminobenzamido*-4-*piperidinophenylarsinic Acid* (V).—Prepared similarly to the preceding one, this *carbamide* was obtained in quantitative yield. It was purified for analysis and physiological testing by dissolving it in 5 volumes of 90% formic acid and adding the solution to 50 volumes of boiling water. On continuing the boiling, the carbamide gradually separated (Found: loss at 100°, 5·8. $C_{37}H_{42}O_9N_6As_2,3H_2O$ requires $3H_2O$, 5·9. Found in the anhydrous acid: As, 17·8. $C_{37}H_{42}O_9N_6As_2$ requires As, 17·4%). This carbamide is soluble in concentrated hydrochloric or formic acid and is precipitated on dilution. It is practically insoluble in boiling glacial acetic acid or 50% formic acid, but its crystalline form may be seen by dissolving it in cold 90% formic acid, adding water until a turbidity is produced, boiling the solution, and continuing the addition of water until the solution is again turbid; on cooling, the carbamide crystallises in microscopic, woolly needles. The amorphous *magnesium*, *calcium*, and *barium* salts are immediately precipitated from dilute ammoniacal solution, and the *sodium* salt is precipitated in amorphous particles by addition of excess of 2*N*-sodium hydroxide to a solution of the sodium salt. The maximum tolerated dose is 0·2 mg.

s-*Carbamide of* 4-*Amino*-2-*hydroxyphenylarsinic Acid* (VI).—The amino-acid (4·7 g. of monohydrate) was phosgenated in the presence of sodium carbonate (10 mols. in 200 c.c. of water) until the reaction was acid. The crystalline precipitate (3·5 g.) was dissolved in dilute ammonia and reprecipitated by acid (yield 3·3 g.) (Found: loss at 100°, 7·6. $C_{13}H_{14}O_9N_2As_2,2H_2O$ requires H_2O, 6·8. Found in anhydrous solid: As, 30·5. $C_{13}H_{14}O_9N_2As_2$ requires As, 30·5%). This carbamide is practically insoluble in boiling acetic or formic acid; it is sparingly soluble in boiling water, and crystallises therefrom in rods. Dilute ammoniacal solutions gave immediate amorphous precipitates with calcium, magnesium, and barium chlorides.

An aqueous or, better, alcoholic solution of the acid gives a port-wine colour on addition of ferric chloride. The maximum tolerated dose is 0·3 mg.

s-*Carbamide of* 5-*Nitro*-4-*amino*-2-*hydroxyphenylarsinic Acid*.—The preceding carbamide (7·0 g.) in 28 c.c. of sulphuric acid was nitrated at 0° with 2·8 g. of nitric acid (*d* 1·42) in 3 c.c. of sulphuric acid. The solution was poured into water, and a yellow, crystalline solid (7·8 g.) slowly separated. When stirred with cold water, this carbamide yields a yellow, opalescent solution. It is readily soluble in boiling water; on cooling, the solution becomes acid to Congo-paper, and gradually becomes limpid with deposition either of the anhydrous *acid*, crystallising in yellow plates, or of the *dihydrate* in fine, yellow needles (Found: loss at 100°, 6·0. $C_{13}H_{12}O_{13}N_4As_2,2H_2O$ requires H_2O, 5·8%). The *magnesium*, *barium*, and *calcium* salts are precipitated amorphous from ammoniacal solution. The *sodium* salt crystallises well and is only moderately easily soluble in water. The *tetra-ammonium* salt is sparingly soluble and crystallises in fine, orange-yellow needles. It is partly hydrolysed by washing with water, as is shown by analysis [Found: loss at 100°, 10·1. $C_{13}H_{12}O_{13}N_4As_2,3\frac{1}{2}NH_3,4H_2O$ requires H_2O, 10·1. Found in the anhydrous salt: volatile NH_3, 8·7; As (Lehmann), 23·3. $C_{13}H_{12}O_{13}N_4As_2,3\frac{1}{2}NH_3$ requires NH_3, 9·3; As, 23·3%].

s-4-*Carbamide of* 4 : 5-*Diamino*-2-*hydroxyphenylarsinic Acid* (VII)—A clear solution of the preceding nitro-compound (1·16 g.) in 12 c.c. of *N*-sodium hydroxide at 0° was treated with 5 g. of sodium hyposulphite, and the external cooling agent simultaneously removed. On stirring for about 2 hours, the precipitated yellow nitro-compound was replaced by the required *amino*-compound. This was collected, dissolved in 11 c.c. of *N*-hydrochloric acid, and precipitated, as an almost white, microcrystalline powder, by addition of sodium acetate (yield 85%) (Found: loss at 100°, 6·9. $C_{13}H_{16}O_9N_4As_2,2H_2O$ requires H_2O, 6·5. Found in dried substance: As, 28·4. $C_{13}H_{16}O_9N_4As_2$ requires As, 28·7%). This amino-acid is readily soluble in dilute mineral acids, but its salts are hydrolysed on dilution. It gives a yellow solution on addition of sodium nitrite but does not couple with alkaline β-naphthol, probably owing to the formation of a soluble diazoimide. The maximum tolerated dose is 0·8 mg.

2-*Hydroxy*-4-*carbamidophenylarsinic Acid* (VIII).—The parent amino-acid (1·35 g.) in 2·5 c.c. of water was treated with 1·74 g. of potassium cyanate (4 mols.); all then passed into solution. After addition of 0·8 c.c. of glacial acetic acid the solution was kept for 24 hours and then made acid (Congo-paper), and the precipitate was collected (yield 1·25 g.). On careful addition of sodium acetate to the filtrate, 0·15 g. of unchanged amino-acid was recovered (Found: loss at 100°, 3·3. $C_7H_9O_5N_2As,\frac{1}{2}H_2O$ requires H_2O, 3·2. Found in dried substance: As, 27·2. $C_7H_9O_5N_2As$ requires As, 27·2%). This acid is soluble in 66 parts of boiling water and crystallises in fine needles. Its ammoniacal solution gives immediate precipitates of the amorphous *magnesium* and *calcium* salts on addition of the respective chlorides, but the *barium* salt, obtained on boiling, is crystalline. The maximum tolerated dose is 0·4 mg.

3 : 5-*Dinitro-2-hydroxyphenylarsinic Acid* (IX).—Picramic acid (10·0 g.) was suspended in 60 c.c. of 3*N*-hydrochloric acid at 0° and diazotised by addition of 3·8 g. of sodium nitrite in 38 c.c. of water. Arsenic trioxide (6·2 g.) in 37·2 c.c. of 2*N*-sodium hydroxide was now added rapidly, and into the still acid solution 2*N*-sodium hydroxide (about 150 c.c.) was run slowly until all the brightly coloured quinone-diazide had disappeared and evolution of nitrogen had ceased. The solution was acidified (Congo-paper) and, after removal of amorphous matter, concentrated at 50°. Two crops (10·15 g. in all) of crude dinitro-acid were obtained which, on two crystallisations from 50 c.c. of boiling water, gave yellow leaflets (yield 8·7 g.), m. p. 244—246° (Benda, *loc. cit.*, gives 237°) (Found: As, 24·7. Calc.: As, 24·3%). This acid, treated with 2*N*-ammonia, gives a sparingly soluble *ammonium* salt, which crystallises from water in needles. The *calcium* and *magnesium* salts are precipitated amorphous from ammoniacal solution, but the *barium* salt is crystalline.

3 : 5-*Diamino-2-hydroxyphenylarsinic Acid* (X).—The preceding dinitro-acid (1·0 g.), dissolved in 10 c.c. of *N*-sodium hydroxide at 0°, was treated with 5 g. of sodium hyposulphite all at once, the external bath being simultaneously removed. The temperature rose to about 30° and on continuing the stirring the *diamino*-compound crystallised in long needles (yield 0·5 g.) [Found: As, 30·8 (Carius), 29·7 (Lehmann). $C_6H_9O_4N_2As$ requires As, 30·2%]. This diamino-acid is very soluble in dilute mineral acids and gives a reddish-brown solution on addition of a trace of nitrite. It reduces ammoniacal silver nitrate solution instantaneously and gives a port-wine colour on addition of potassium dichromate solution. The maximum tolerated dose is 0·04 mg.

Nitration of ON-*Diacetyl-2-aminophenol.*—(a) *By nitric acid.* Ten g. of the diacetyl compound were nitrated as described by Meldola, Woolcott, and Wray (*loc. cit.*) and Ingold and Ingold (*loc. cit.*). On dilution with ice *N*-acetylpicramic acid was obtained, m. p. 203°, in 63% yield. On crystallisation from much boiling water it separated in soft, yellow needles, m. p. 205—206°. Its identity was proved by the melting points of its mixture with monoacetylpicramic acid and of mixtures of its acid hydrolytic product with picramic acid and of its diacetylated derivative with *ON*-diacetylpicramic acid. ON-*Diacetylpicramic acid* is readily obtained by boiling picramic or monoacetylpicramic acid with acetic anhydride and a few drops of pyridine. It crystallises from 5 volumes of boiling acetic acid in needles, m. p. 190—191°. *N*-Acetylpicramic acid is obtained by allowing picramic acid to react at room temperature with a small volume of acetic anhydride.

(b) *By nitric acid in sulphuric acid.* Anhydrous *ON*-diacetylaminophenol (9·7 g.) was dissolved at − 5° in 40 c.c. of sulphuric acid and nitrated by the gradual addition of 5 g. of nitric acid (*d* 1·42) mixed with 2·5 c.c. of sulphuric acid. On pouring the solution on ice, 9·0 g. of crude nitration products separated, and ether extraction of the mother-liquor gave 1·1 g. of highly coloured gum. The main crop of solid was hydrolysed by 10% hydrochloric acid and gave, on dilution and partial neutralisation, 3·3 g. of picramic acid. On neutralisation to Congo-paper, the mother-liquor gave 0·9 g. of 4-nitro-2-aminophenol, m. p. 140° (anhydrous) and not depressed by admixture with pure 4-nitro-2-aminophenol. Ether extraction of the final liquors gave 1·05 g., which, on acetylation, gave 1·1 g., m. p. 266°; this, on crystallisation from 45 c.c. of alcohol, gave 0·75 g., melting, alone or mixed with 4-nitro-2-acetamidophenol, at 280°. The aqueous liquors from the acetylation deposited 0·05 g., m. p. 178°, which, on crystallisation from alcohol, gave 4-nitro-*ON*-diacetylaminophenol; this, alone or mixed with a genuine sample of 4-nitrodiacetylaminophenol, melted at 184°. These yields indicate a 66% conversion of the available nitric acid into dinitro-derivative (picramic acid) and a 17·5% conversion into mononitro-derivative.

(c) *By nitric acid in acetic anhydride.* Following Ingold and Ingold (*loc. cit.*), 14·5 g. of diacetyl-2-aminophenol were nitrated in acetic anhydride at 10°. *ON*-Diacetyl-3-nitro-2-aminophenol (1·45 g.) separated in diamond-shaped plates; the product obtained by pouring the mother-liquor into water was fractionally crystallised from alcohol, giving *ON*-diacetyl-5-nitro-2-aminophenol. The 3-nitro-derivative (1·0 g.) was hydrolysed by boiling it with 3*N*-hydrochloric acid and gave, on removal of the acidity to Congo-paper, 0·55 g. of 3-*nitro-2-aminophenol*; this was soluble in 100 parts of boiling water and crystallised in red needles, m. p. 216—217° (Found: C, 46·2; H, 3·9. $C_6H_6O_3N_2$ requires C, 46·7; H, 3·9%). It gave an intense red colour on addition of alkali.

A comparison of the relative colour intensities of 0·2% solutions of 3-, 4-, 5-, and 6-nitro-2-aminophenols in 0·5*N*-sodium hydroxide by means of the Lovibond tintometer gave the following values :

	3-*Nitro.*	4-*Nitro.*	5-*Nitro.*	6-*Nitro.*
Red	36	16	31	15
Yellow	11	18	14	15

Definite maxima of redness which control the general visible intensity are thus found for the two compounds which are *m*-nitrophenols. It thus appears that the chromophoric character in alkaline solution of the *o*- and *p*-nitroaniline groups may be greater than that of the *o*- and *p*-nitrophenolic groups.

Nitration of N-*Acetyl-2-aminophenol.—By nitric acid in acetic anhydride.* A solution of monoacetyl-2-aminophenol (1·5 g.) in 50 c.c. of acetic anhydride at 80° was cooled to 30°, and nitric acid (0·5 c.c.; *d* 1·5) in 2·5 c.c. of acetic anhydride then slowly added. On cooling, there separated 0·5 g. of 4-nitro-2-acetamidophenol, m. p. 279—280°. In admixture with an authentic specimen and with 5-nitro-2-acetamidophenol, this melted at 279—280° and at 245°, respectively. The mother-liquor, on concentration at 70°, gave no further deposit. It was therefore evaporated twice with water at 50°, the residue hydrolysed by boiling for 1 hour with 3*N*-hydrochloric acid, and the solution neutralised (Congo-paper). The brown solid (0·4 g.), m. p. about 100°, thus obtained was ground with *N*-hydrochloric acid, and water gradually added to dissolve the crystalline hydrochloride. The insoluble red solid (0·05 g.) was picramic acid, m. p. 165°, mixed m. p. with pure picramic acid 167°. The soluble fraction, on neutralisation at 80°, gave 0·35 g. of 6-nitro-2-aminophenol; this crystallised in long, maroon-coloured needles, m. p. 112—113°, and its properties agreed with those described for 6-nitro-2-aminophenol by Benda (*Ber.*, 1914, 47, 1010), except that it gave a red and not a blue solution when diazotised and added to R-salt; with alkaline β-naphthol, it gave a purple precipitate. The original aqueous liquors were neutralised (litmus), and extracted with ether; this removed 0·25 g. of unchanged 2-aminophenol which, alone or mixed with pure 2-aminophenol, melted at 174°.

Action of Sulphuric Acid on ON-*Diacetyl-2-aminophenol.*—A solution of 1 g. of *ON*-diacetyl-2-aminophenol in 2 c.c. of sulphuric acid at 10—15° was, after 1 hour, diluted with ice; extraction with ether than gave *N*-acetyl-2-aminophenol in almost quantitative yield.

Action of Nitric Acid on ON-*Diacetyl-2-aminophenol at* — 5°.—One g. of diacetylaminophenol was dissolved in a mixture of 4 c.c. of nitric acid (*d* 1·42) and 2 c.c. (*d* 1·5) at — 5° and kept at this temperature for ½ hour. When the solution was mixed with ice, 0·5 g. of unchanged diacetyl-2-aminophenol separated; ether extraction of the mother-liquor gave a further 0·15 g. containing traces of nitrated products.

The thanks of the author are due to Mr. W. K. Anslow for help in the preparations and analyses.

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HAMPSTEAD. [*Received, March 18th, 1927.*]

CXLIII.—*The Properties of Conjugated Compounds. Part II. Addition to Butadiene Esters.*

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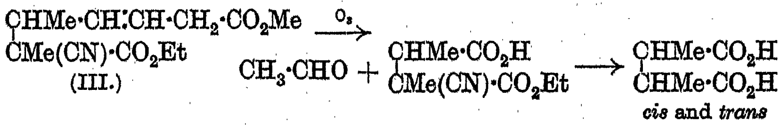
IT has been established that the addition of esters to αβ-unsaturated esters and ketones can take place reversibly in two ways, yielding products of the normal and the abnormal type $\cdot CHX\cdot CH_2\cdot CO$ and $CH_2\cdot CHX\cdot CO$ [$X=CH(CO_2Et)_2$, etc.], respectively, although generally one type of addition may be favoured to the practical exclusion of the other. The formation of one or other (or both) of the additive products in a given case is dependent on a system of connected equilibria which vary with the experimental conditions but are not greatly affected by the polar condition of the reactants (compare E. H. Ingold, J., 1925, **127**, 469; Cooper, Ingold, and Ingold, J., 1926, 1868). With conjugated esters of the type $CH{:}CH\cdot CH{:}CH\cdot C{:}O$, however, the possible modes of additive reaction are more numerous. Vorländer, in securing the attachment of the malonic residue at the δ-carbon atom of methyl sorbate (*Annalen*, 1906, **345**, 227), experimentally demonstrated that they are not confined to αβ-addition, and it is possible that attachment of the components of the addendum may occur simultaneously or alternately in two or more ways.

In seeking evidence of the variability or otherwise of addition to butadiene derivatives, the additive properties of sorbic and β-vinylacrylic acids were studied. The addition of methyl sodiomalonate to the esters of these acids has recently been examined by Kohler and Butler (*J. Amer. Chem. Soc.*, 1926, **48**, 1036), who obtained in the respective cases excellent yields of the compounds $(MeO_2C)_2CH\cdot CHMe\cdot CH{:}CH\cdot CH_2\cdot CO_2Me$ (I) and

$(MeO_2C)_2CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CO_2Me$ (II),

which appeared to be the sole products of addition. Our experiments, carried out before the appearance of Kohler and Butler's paper, gave results concerning the formation and constitution of these compounds in complete agreement with those of the latter authors, and in the case of methyl β-vinylacrylate, particularly, the absence of any but the minutest traces of a second additive product was readily demonstrable. Further, an examination of (II) showed it to be non-mobile : it neither suffered double-bond displacement by the action of sodium methoxide nor showed any tendency to undergo further condensation with esters like methyl cyanoacetate. Therefore its formation by a process of γδ-addition—a possibility not usually considered but which would be somewhat analogous to the formation of γ-oxalyl derivatives of ββ-dimethylacrylic ester (Higginbotham and Lapworth, J., 1923, **123**, 1325)—followed by double-bond displacement is out of the question. The additions are indubitably and completely of αδ-type.

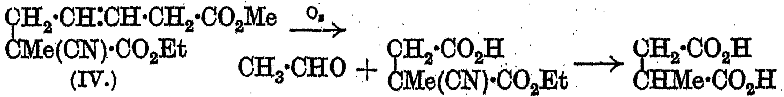
Attempts to obtain a different result by varying the experimental conditions of condensation failed entirely, but the limits of variation with substances so prone to polymerisation as sorbic and β-vinylacrylic esters were necessarily narrow. Attention was therefore directed to the effect of varying the ester-addendum, as, for instance, by alkylation. Few cases of the employment of alkylated malonic and cyanoacetic esters in the Michael reaction are recorded in the literature. Thorpe observed (J., 1900, **77**, 932) that during reaction between ethyl ββ-dimethylacrylate and ethyl methylsodiocyanoacetate the addendum appeared to suffer an unusual partition, $\text{CH}_3\text{—}\vdots\text{—C(CN)}{:}\text{C(ONa)}\cdot\text{OEt}$, leading to the formation of the methylable sodio-derivative of an ester $\text{EtO}_2\text{C}\cdot\text{CHMe}\cdot\text{CMe}_2\cdot\text{CH(CN)}\cdot\text{CO}_2\text{Et}$. E. H. Ingold has interpreted the observations of Bone and Sprankling (J., 1899, **75**, 839) concerning the interaction of ethyl ethylsodiomalonate and ethyl α-bromo*iso*butyrate in a manner involving reversible Michael additions, whereby the effect of the alkyl group of the addendum is to favour the abnormal type of αβ-addition. With both sorbic and β-vinylacrylic esters, however, the addition of ethyl methylcyanoacetate, which readily takes place, follows the same course as with ethyl malonate; the esters (III) and (IV) are exclusively produced in the respective cases, the constitutions following from the nature of the ozone degradation products as shown below.



$$\begin{array}{l}\text{CHMe}\cdot\text{CH}{:}\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}\\ \text{CMe(CN)}\cdot\text{CO}_2\text{Et}\end{array} \xrightarrow{\text{O}_3} \text{CH}_3\cdot\text{CHO} + \begin{array}{l}\text{CHMe}\cdot\text{CO}_2\text{H}\\ \text{CMe(CN)}\cdot\text{CO}_2\text{Et}\end{array} \longrightarrow \begin{array}{l}\text{CHMe}\cdot\text{CO}_2\text{H}\\ \text{CHMe}\cdot\text{CO}_2\text{H}\end{array}$$

(III.)

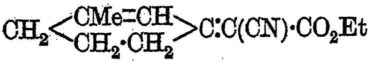
cis and *trans*



$$\begin{array}{l}\text{CH}_2\cdot\text{CH}{:}\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}\\ \text{CMe(CN)}\cdot\text{CO}_2\text{Et}\end{array} \xrightarrow{\text{O}_3} \text{CH}_3\cdot\text{CHO} + \begin{array}{l}\text{CH}_2\cdot\text{CO}_2\text{H}\\ \text{CMe(CN)}\cdot\text{CO}_2\text{Et}\end{array} \longrightarrow \begin{array}{l}\text{CH}_2\cdot\text{CO}_2\text{H}\\ \text{CHMe}\cdot\text{CO}_2\text{H}\end{array}$$

(IV.)

Indeed in no experiment could any divergence from the type of ester-addition be observed, and in particular there is little doubt of the entire absence of αβ-products. Consequently, any representation such as that of Kohler and Butler (1 : 4-additive product $\rightleftharpoons$ $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me$ + $Na[CH(CO_2Me)_2]$ $\rightleftharpoons$ 1 : 6-additive product) is at present purely speculative. In view of the foregoing results, the observation that ethyl methyl*cyclo*hexenylidenecyanoacetate (V) under Guareschi's conditions adds on the components of

(V.) 

$$CH_2{<}\begin{matrix}CMe{=}CH\\CH_2{\cdot}CH_2\end{matrix}{>}C{:}C(CN){\cdot}CO_2Et$$

$CH_3{\cdot}CH{:}CH{\cdot}CH{:}C(CO_2Et)_2$ (VI.)

ethyl cyanoacetate at the αβ-carbon atoms (Farmer and Ross, J., 1926, 1577) is of interest; this substance may be regarded as a substituted sorbic ester in which both spatial and polar conditions are modified—a modification which causes complete change of additive mode. With the α-carboxysorbic ester (VI) addition of esters could not be secured.

It was shown by Auwers and Heyna (*Annalen*, 1923, **434**, 140) that sorbic acid adds on bromine at the γδ-double bond. β-Vinylacrylic acid behaves similarly. The crude dibromide consisted of a mixture of crystalline and liquid material, each portion of which yielded with diethylamine a crystalline bromovinylacrylic acid. The identity or otherwise of these two products could not be satisfactorily determined, since both polymerised on heating and neither could be satisfactorily reduced. The bromination product was, however, constitutionally homogeneous, both solid and liquid portions yielding acraldehyde dibromide (identified by conversion into α-bromoacraldehyde) and oxalic acid. No trace of material derived by αβ- or βγ-addition could be isolated.

EXPERIMENTAL.

A. Derivatives of β-Vinylacrylic and Sorbic Acids.

β-Vinylacrylic acid, prepared by Doebner's method (*Ber.*, 1902, **35**, 1137), was purified by solution in ether and extraction with dilute aqueous sodium carbonate. The acid obtained by re-extracting the alkaline liquid was drained on porous tiles and recrystallised from petroleum. It formed colourless, prismatic needles, m. p. 80° (Doebner, m. p. 80°; Kohler and Butler, m. p. 72°).

The *dibromide* was obtained in the usual way, carbon disulphide being used as diluent. The crude product, thoroughly freed from carbon disulphide, partly solidified when cooled in an ice–salt mixture. The semi-solid mass was spread on porous tiles; these absorbed the oily matter, leaving a solid which separated from petroleum in tufts of colourless needles, m. p. 47° (Found: Br, 61·55. $C_5H_6O_2Br_2$ requires Br, 62·0%). The *methyl* ester, obtained by the action of methyl alcohol and sulphuric acid on the solid dibromide, was a pale yellow oil, b. p. 136°/10 mm. (Found: Br, 58·6. $C_6H_8O_2Br_2$ requires Br, 58·8%).

Extraction of the porous tiles with ether yielded a brown oil (about one-fifth of the total product) from which no further solid matter could be obtained. From this dibromo-acid (Found: Br, 61·6%), which was examined separately, the *methyl* ester was obtained as a pale yellow oil, b. p. 134—136°/12 mm. (Found: Br, 59·1%).

Bromo-β-vinylacrylic Acid.—The solid dibromide (10 g.), dissolved in absolute ether (150 c.c.), was gradually treated with an ethereal solution of diethylamine (8 g.) at 0°. Diethylamine hydrobromide separated rapidly; when separation had ended, the ethereal liquor was filtered, agitated several times with dilute sulphuric acid, and finally dried. Removal of the solvent yielded an acid which crystallised from benzene–petroleum in long, colourless needles (Found: Br, 44·9. $C_5H_5O_2Br$ requires Br, 45·2%). When this substance was heated, it changed without melting or evident degradation to a yellow, apparently amorphous, solid which gradually darkened in colour as the temperature rose. A similar yellow solid, doubtless a polymeride of bromovinylacrylic acid, was obtained when boiling pyridine was employed in place of diethylamine. Pure crystalline bromovinylacrylic acid could not be kept; invariably it changed, in less than 2 days, to a brown, amorphous mass. The *methyl* ester, obtained in similar fashion from the ester of the solid portion of the dibromide (above), was a pale yellow oil which solidified on cooling to 0° (m. p. about 10°), but polymerised to a thick jelly on standing for 2 hours at room temperature.

Removal of hydrogen bromide from the liquid portion of the dibromide (using ethereal diethylamine) yielded a bromovinylacrylic acid which crystallised from benzene–petroleum in colourless plates (Found: Br, 44·9%). When heated, this acid behaved like the above described monobromo-acid; when allowed to stand, the crystalline form was gradually lost, the change becoming marked after 7—8 days. The *methyl* ester obtained in a similar way from the ester of the liquid portion of the dibromide (above) was a yellow oil, b. p. 95—98°/16 mm., which polymerised within 8 hours of distillation (Found: Br, 41·7. $C_6H_7O_2Br$ requires Br, 41·9%). Attempts to establish the identity of the two specimens of bromovinylacrylic acid did not succeed; reduction to vinylacrylic acid could not be effected.

Sorbic Acid Dibromide.—Bromination of sorbic acid yielded a crude dibromide which consisted of a solid, m. p. 94—95°, and a yellow liquid (compare Kachel and Fittig, *Annalen*, 1873, **168**, 287; Auwers and Heyna, *loc. cit.*). From the liquid, however, further large quantities of the solid dibromide separated, and it is probable that the very small liquid residue consisted almost entirely of the solid form, since it did not yield a distinctive bromosorbic acid on treatment with diethylamine. Esterification of the solid dibromide yielded the *methyl* ester, a pleasant-smelling liquid, b. p. 146°/12 mm. (Found: Br, 56·0. $C_7H_{10}O_2Br_2$ requires Br, 55·9%). The same compound was obtained by addition of bromine to pure methyl sorbate.

Bromosorbic acid was obtained by treating an ethereal solution of solid sorbic acid dibromide with diethylamine. It crystallised from benzene–petroleum in white plates, m. p. 140° (Found: Br, 41·8. $C_6H_7O_2Br$ requires Br, 41·9%). The *methyl* ester of this acid was obtained in similar fashion from the methyl ester of solid sorbic acid dibromide (above). It was a pleasant-smelling, yellow oil, b. p. 104—106°/10 mm. (Found: Br, 38·8. $C_7H_9O_2Br$ requires Br, 39·0%).

Removal of hydrogen bromide from the small liquid residue obtained in the bromination of sorbic acid yielded a bromosorbic acid, m. p. 140°, identical with that described above.

Reduction of Bromosorbic Acid.—When this acid was reduced in the usual way with zinc dust and acetic acid, a halogen-free, brown oil was obtained which soon solidified. After recrystallisation, it melted at 140° and was identical with ordinary sorbic acid. To avoid geometrical inversion which had possibly occurred, milder reducing agents were tried, but reduction could not be effected therewith.

B. Addition of Esters.

Methyl β-methyl-Δ^{γ}-pentene-ααε-tricarboxylate was obtained, in 60—70% yield, by addition of methyl malonate to methyl sorbate under essentially the conditions described by Kohler and Butler (*loc. cit.*). The ester corresponded in boiling point with that obtained by Kohler and Butler.

Condensation was also attempted under other conditions. Employment of an ethereal, alcohol-free suspension of ethyl sodiomalonate with methyl sorbate at room temperature yielded a product containing methyl methylpentenetricarboxylate, products derived therefrom by internal condensation, and polymeric products from methyl sorbate. With diethylamine as condensing agent and methyl cyanoacetate as addendum, no addition occurred; there was a similar result when these substances were brought together under Guareschi's conditions. When alcoholic methyl sodiomalonate was employed, subsidiary condensations proceeded too far to allow isolation of any pure product.

Methyl Δ^{γ}-pentene-ααε-tricarboxylate was obtained in a similar way by adding methyl malonate to methyl β-vinylacrylate. This ester, prepared by esterification of the pure acid with methyl alcohol and sulphuric acid, could be stabilised for a considerable time by addition of a small quantity of quinol immediately after distillation. In most of the condensations no appreciable quantity of the latter ester was recovered unchanged. The addition product distilled at 178—180°/17 mm. (172°/13 mm. on redistillation. Kohler and Butler give a lower b. p., 147—151°/11 mm.). The *triamide* was formed in almost quantitative yield when the ester was allowed to stand with alcoholic ammonia. It formed colourless prisms, m. p. 213° (Found: C, 48·5; H, 6·7. $C_8H_{13}O_3N_3$ requires C, 48·2; H, 6·5%).

Methyl Ethyl β-Cyano-γ-methyl-Δ^δ-hexene-βζ-dicarboxylate.—To a solution of sodium (2·3 g.) in the minimal quantity of absolute methyl alcohol, ethyl methylcyanoacetate (12·8 g.) and sufficient dry ether to produce a permanent turbidity were added. Methyl sorbate (12·6 g.) was then dissolved in the solution, and the whole refluxed on a steam-bath for 6 hours. More ether was added to the cooled product, which was then poured into water and worked up in the usual way. The oil so obtained yielded unchanged esters and a product (2 g.) of b. p. 185—188°/16 mm. In each of three such additions, a similar yield was obtained. When, however, only one-eighth of the sodium theoretically required was used and the refluxing continued for 5 hours, the yield of addition product rose to 60—70%. The latter was a pale yellow, mobile oil (Found: C, 61·8; H, 7·4. $C_{13}H_{19}O_4N$ requires C, 61·6; H, 7·5%).

Methyl ethyl β-cyano-Δ^δ-hexene-βζ-dicarboxylate was prepared in similar fashion to the preceding ester, ethyl methylcyanoacetate (2 mols.), methyl β-vinylacrylate (1 mol.), and sodium (1/8 atom) being used. Refluxing for more than 5 hours resulted in a diminished yield. The ester was a pale yellow, mobile oil, b. p. 182—185°/16 mm. (Found: C, 60·3; H, 7·0. $C_{12}H_{17}O_4N$ requires C, 60·25; H, 7·1%).

Attempted Addition of Esters to Methyl Δ^γ-Pentene-ααε-tricarboxylate.—In order to ascertain the mobility or fixity of the double bond in methyl pentenetricarboxylate, attempts were made to secure addition of methyl cyanoacetate, (1) using sodium as condensing agent under the conditions described above, and (2) under Guareschi's conditions. In neither case did addition take place.

Attempted Addition of Methyl Malonate and Methyl Cyanoacetate to Methyl Crotonylidenemalonate.—Methyl crotonylidenemalonate was synthesised by the method of Meerwein (*Annalen*, 1908, **358**, 82). All attempts by the above-described methods to secure its condensation with methyl malonate failed. Condensation with methyl cyanoacetate under Guareschi's conditions also did not succeed. Attempts to prepare by Meerwein's method the probably more reactive methyl crotonylidenecyanoacetate were unsuccessful.

C. *Oxidations.*

Ozonisation of Vinylacrylic Acid Dibromide.—Through a solution of the solid dibromide (10 g.) (p. 1062) in 60 c.c. of chloroform, mixed with 10 c.c. of water, a rapid stream of ozonised oxygen was passed for 6 hours. The issuing gases were led through aqueous ammonia to absorb any formaldehyde carried from the decomposition vessel. The absence of formaldehyde was demonstrated by the hexamethylenetetramine test. The aqueous and the chloroformic layer were separated. A portion of the former, acidified with acetic acid, yielded with calcium chloride a thick precipitate of calcium oxalate; from the remainder a quantity of pure oxalic acid was isolated. The chloroformic layer was evaporated at room temperature. The residue, a pale yellow oil, was warmed for ½ hour with aqueous potassium acetate (8 g. in 12 c.c. of water). The deep yellow, lachrymatory *α-bromoacraldehyde* so produced was distilled in steam and extracted with ether; it was obtained, after removal of the solvent and distillation, as a pale yellow oil, b. p. 58°/21 mm. (Found: Br, 59·2. C_3H_3OBr requires Br, 59·25%). It yielded a *semicarbazone*, m. p. 160°, which was identical with that obtained from a specimen of α-bromoacraldehyde synthesised by the method of Auwers and Heyna (*loc. cit.*).

The liquid dibromide also was oxidised in a similar way and yielded the same degradation products. No compounds arising from αβ- or αδ-dibromides could be found among the oxidation products.

Ozonisation of Methyl Methylpentenetricarboxylate (I) *and Methyl Pentenetricarboxylate* (II).—The oxidation of these substances was conducted in a similar way to that described by Kohler and Butler (*loc. cit.*) and yielded precisely similar results.

Ozonisation of Methyl Ethyl Cyanomethylhexenedicarboxylate (III).—The ester (10 g.), dissolved in dry chloroform (30 c.c.), was submitted to a current of ozonised oxygen for 36 hours. On evaporation of the chloroform under diminished pressure, the ozonide was obtained as a viscous, faintly yellow oil. This was decomposed by heating with water (30 c.c.) for 2 hours, the escaping vapours being passed into a solution of *p*-nitrophenylhydrazine hydrochloride. The yellow precipitate (m. p. 126° after recrystallisation) which formed in the latter was identified as acetaldehyde-*p*-nitrophenylhydrazone by comparison with an authentic specimen.

The aqueous liquor was mixed with 30% hydrogen peroxide

(50 c.c.). After 12 hours, the aqueous portion was decanted, and the oil hydrolysed by boiling with 40% potassium hydroxide solution (30 c.c.) until no more ammonia was evolved (5 hours). The cooled alkaline liquid yielded, on acidification and extraction, a gummy acid which partly crystallised. This was esterified with alcohol and sulphuric acid and distilled. The colourless ester, b. p. 125—132°/12 mm., was re-hydrolysed with alcoholic potassium hydroxide; a solid potassium salt separated which yielded an acid, m. p. 123°, and the alcoholic liquor yielded a second acid, m. p. 195°. These acids were identified by their basicity and by comparison with authentic specimens as *cis*- and *trans*-forms, respectively, of *s*-dimethylsuccinic acid.

Ozonisation of Methyl Ethyl Cyanohexenedicarboxylate (IV).—The method was that employed in the preceding oxidation. The only substances that could be isolated were acetaldehyde (identified as the *p*-nitrophenylhydrazone, m. p. 126°) and a cyano-ester which yielded a considerable quantity of methylsuccinic acid, m. p. 112° (identified by basicity and comparison with an authentic specimen).

The authors desire to acknowledge grants from the Government Grant Committee of the Royal Society (to E. H. F.) and the Chemical Society (to A. T. H.) towards the expenses of this research.

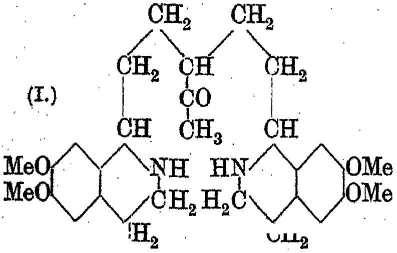
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, January 31st,* 1927.]

CXLIV.—*The Alkaloids of Ipecacuanha. Part IV.*

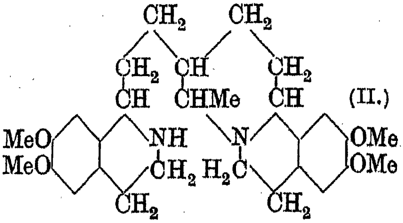
By WILLIAM HARRISON BRINDLEY and FRANK LEE PYMAN.

IN the earlier parts of this series (Carr and Pyman, J., 1914, **105**, 1591; Pyman, Part II, J., 1917, **111**, 419; Pyman, Part III, J., 1918, **113**, 222), the formula $C_{29}H_{40}O_4N_2$ was established for emetine, and Hesse's observation (*Pharm. J.*, 1898, **7**, 98) that it contains four methoxyl groups, and Keller's discovery (*Arch. Pharm.*, 1911, **249**, 512) that it is a secondary-tertiary base, were confirmed. The relations of emetine to its subsidiary alkaloids were determined, and many reactions of these bases were described. It was shown that emetine is a derivative of *iso*quinoline, since it gave 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid on oxidation.

Some two years ago, Professor Robert Robinson, F.R.S., suggested, on the basis of a theory of structural or genetic relationships of alkaloids of the *iso*quinoline group, that emetine and its congeners might be derived from two molecules of dihydroxyphenylalanine, two molecules of glyceraldehyde, and one molecule of dihydroxy-acetone by processes of condensation, decarboxylation, methylation, and reduction. Coming closer to normal laboratory syntheses in order to simplify the discussion, one might imagine the condensation of two molecules of acraldehyde and one molecule of acetone to the ketone-dialdehyde,* $(CHO{\cdot}CH_2{\cdot}CH_2)_2CH{\cdot}CO{\cdot}CH_3$, and the subsequent condensation of this intermediate with β-(3 : 4-dimethoxyphenyl)ethylamine to the *iso*quinoline derivative (I).



(I.)



(II.)

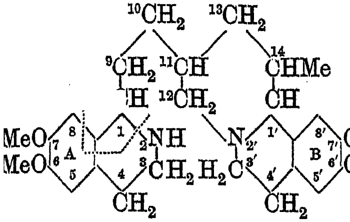
On reduction and dehydration, (II) is obtained, and this, it was thought, might be the constitution of emetine. Recently, this field of work has been entered by Späth and Leithe (*Ber.*, 1927, **60**, 688), who have put forward a partial formula for emetine in harmony with the above formula (II), in that it contains two dimethoxy-*iso*quinoline residues connected through the 1-position in each case. It has consequently become necessary to publish Robinson's formula at once. Whilst this formula is able to afford an explanation of most of the salient facts in the chemistry of the alkaloids related to emetine, there is undoubtedly a difficulty in connexion with the nature of rubremetine.

Oxidation of emetine with ferric chloride, bromine, or iodine, or of *O*-methylpsychotrine with bromine or iodine, yields the deep red rubremetine salts, *e.g.*, rubremetinium chloride, $C_{29}H_{33}O_4N_2Cl$, in which one of the nitrogen atoms has lost its basicity and the other has become quaternary (Carr and Pyman; Pyman, Part II, *loc. cit.*; Karrer, *Ber.*, 1916, **49**, 2057).

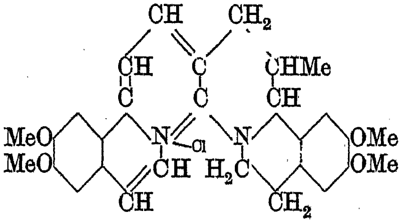
It would appear, therefore, that the removal of eight hydrogen atoms from emetine in the process of oxidation to rubremetine should be accompanied by some structural change which could destroy the salt-forming power of one of the nitrogen atoms. This would hardly be the case with rubremetine formulæ derived from (II) by simple oxidation of two of the three hydrogenated pyridine rings, and in this respect Robinson's formula for emetine seems to us unsatisfactory. It has led us, however, to put forward a formula

* The type $R_2CH{\cdot}CO{\cdot}CH_3$ was preferred to $R{\cdot}CH_2{\cdot}CO{\cdot}CH_2R$ because cuskhygrine is a representative of the former class.

for emetine (III), differing from Robinson's only in the position of the *C*-methyl group, which affords a convincing explanation of the formation of rubremetine (IV), and is equally satisfactory in other respects.



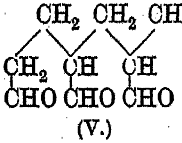
Emetine (III.)



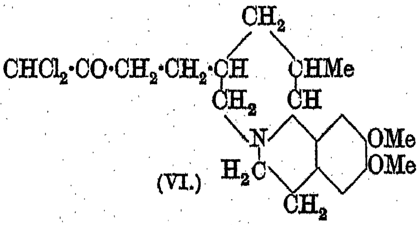
Rubremetinium chloride (IV.)

The loss of basicity of one of the nitrogen atoms in the conversion of emetine into rubremetine is thus attributed to amidine formation, a double bond connecting N(2) with C(12). Evidence is given below that *O*-methylpsychotrine, and therefore probably rubremetine also, contains a double bond between C(1) and C(9), and this necessitates a third double bond between C(10) and C(11) to complete the unsaturation of the new ring. The fourth double bond is assumed to lie between C(3) and C(4), thus giving the berberine-like structure for rubremetine shown above. This formula accords with the facts that rubremetine cannot be converted into derivatives analogous to oxyberberine or berberine-acetone. It is also in harmony with the fact that no substance analogous to rubremetine can be made by the oxidation of *N*-methylemetine with bromine.

Turning to the new formula for emetine (III) itself, it may be pointed out that the skeleton of this formula might be produced phytochemically by the condensation of two molecules of dihydroxyphenylalanine with a condensation product (V) derived from three molecules of glyceraldehyde.



(V.)



(VI.)

This process leads to two alternative formulæ for emetine, namely, (III), and a second formula in which the *C*-methyl group is attached to C(9) instead of C(14), but formula (III) is preferred for reasons given later. It may be pointed out, however, that in both formulæ this methyl group is shown in a position relative to an *iso*quinoline ring, which it is known to occupy in other alkaloids, for example, corydaline.

The new formula for emetine permits the deduction of intelligible formulæ for the subsidiary alkaloids of ipecacuanha.

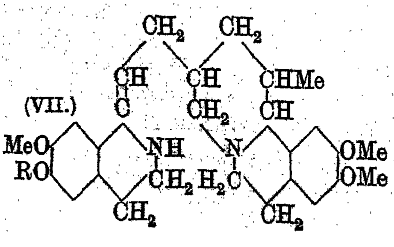
Cephæline, $C_{28}H_{38}O_4N_2$, contains a phenolic hydroxyl group in the place of one of the methoxy-groups of emetine, and yields emetine on methylation. It yields on oxidation with ferric chloride a base, $C_{20}H_{27}O_3NCl_2$, from which no nitrosoamine could be prepared, containing two methoxy-groups, and two chlorine atoms which were readily replaceable by hydroxyl (Carr and Pyman, *loc. cit.*), giving a compound $C_{20}H_{29}O_5N$, which appeared to have amphoteric character. The base $C_{20}H_{27}O_3NCl_2$ contains only one benzene nucleus (Dobbie and Fox, J., 1914, **105**, 1639), whence it follows that the benzene nucleus containing the phenolic hydroxyl group has been eliminated, together with one of the nitrogen atoms. The only explanation of the formation of the base $C_{20}H_{27}O_3NCl_2$ which seems to us plausible is indicated by dotted lines in the emetine formula (III), and leads to the conclusion that the phenolic hydroxyl group of cephæline must be placed in ring A, probably in position 6 of the *iso*quinoline ring. The choice of position 6 for this hydroxyl group is confirmed by evidence discussed below in connexion with psychotrine.

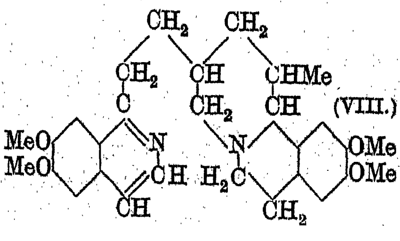
The properties of the base $C_{20}H_{27}O_3NCl_2$ are expressed by the formula (VI). Its conversion into the substance $C_{20}H_{29}O_5N$ by means of cold aqueous sodium hydroxide may be attributed to the formation of a substituted glyoxal, which then undergoes a change resembling the transformation of methylglyoxal into lactic acid. The substance $C_{20}H_{29}O_5N$ thus has the formula (VI) with

$$\cdot CH(OH)\cdot CO_2H$$

in place of $\cdot CO\cdot CHCl_2$.

Psychotrine, $C_{28}H_{36}O_4N_2$ (VII, R = H), yields on reduction cephæline and a stereoisomeride *iso*cephæline. *O*-Methylpsychotrine, $C_{29}H_{38}O_4N_2$ (VII, R = Me), yields on reduction emetine and *iso*emetine. They, therefore, contain a double linking, and saturation of this renders (at least) one additional carbon atom asymmetric (Carr and Pyman; Pyman, Parts II and III, *locc. cit.*) :


(VII.)


(VIII.)

This condition can be fulfilled in many ways, but it is shown below that *O*-methylpsychotrine gives a good yield of psychotrine on partial hydrolysis with one molecule of acid. One of the four methoxy-groups is thus preferentially hydrolysed, and it must be in ring A, since cephæline, and therefore psychotrine, contains hydroxyl in this ring. It is suggested that the cause of the preferential hydrolysis is the presence of a double bond between C(1) and C(9), and that the methoxy-group in the para-position to the substituted vinyl group has become hydrolysed.

Confirmation of the situation of the double linking in the $\alpha\beta$-position to a benzene nucleus is afforded by the fact that *O*-methylpsychotrine yields on reduction, besides emetine and *iso*emetine, a demethoxyemetine or demethoxy*iso*emetine (base C, Part II, *loc. cit.*) in which one of the methoxy-groups has been replaced by hydrogen, for there is evidence (Semmler, *Ber.*, 1908, **41**, 2556; Salway, J., 1910, **97**, 2413) that a substituted vinyl group facilitates the replacement by hydrogen of alkyloxy-groups situated in the para-position with respect to it. The deep yellow colour of psychotrine base is also in accord with formula (VII).

The reason why formula (III) for emetine is preferred to that in which the *C*-methyl group is attached to C(9) is that *O*-methylpsychotrine gives emetine and *iso*emetine in fair yield on reduction, in spite of the complications introduced by demethoxylation, and it is therefore considered probable that only one additional carbon atom is rendered asymmetric by the reduction, giving two isomerides, whereas the alternative formula requires the rendering of two additional carbon atoms asymmetric, thus giving four possible isomerides.

Emetamine, $C_{29}H_{36}O_4N_2$ (VIII), is a ditertiary base yielding on reduction a mixture from which a small quantity of *iso*emetine can be isolated as benzoyl derivative. Emetamine is more feebly basic than *O*-methylpsychotrine (Pyman, Part II, *loc. cit.*), and may be regarded as containing the *iso*quinoline ring A in the unsaturated condition. Formula (VIII) accords with the facts that (1) although emetamine contains two atoms of hydrogen fewer than *O*-methylpsychotrine, it is not formed in the incomplete oxidation of *O*-methylpsychotrine to rubremetine, and (2) it cannot be converted into rubremetine.

The purity of the preparation of emetamine described in Part II has now been confirmed by the fractionation of a considerable quantity of this base, which has been characterised further by the preparation of a number of salts.

EXPERIMENTAL.

O-Methylpsychotrine has now been crystallised. It separates from hot dry ether in well-formed prisms, m. p. 123—124° (corr.) (Found: C, 73·0; H, 8·3. $C_{29}H_{38}O_4N_2$ requires C, 72·7; H, 7·9%). It is sparingly soluble in hot dry ether, almost insoluble in cold dry ether, but readily soluble in cold alcohol. In commercial absolute alcohol it had $[\alpha]_D + 43{\cdot}2°$ ($c = 1$); $[\alpha]_D + 43{\cdot}4°$ ($c = 2{\cdot}1$); $[\alpha]_D + 43{\cdot}2°$ ($c = 3{\cdot}9$).

O-Methylpsychotrine picrate crystallises from acetone in octagonal plates which, after being dried at 100°, soften from 142° and gradually melt up to 175° (corr.).

Oxidation of O-Methylpsychotrine.—(1) *By permanganate.* The base from 6 g. of methylpsychotrine hydrogen oxalate in acetone (150 c.c.) was oxidised by the addition of a saturated aqueous solution of potassium permanganate (35 g.) in the course of ½ hour with thorough stirring, the temperature of the solution rising from 16° to 24°. After the products had been worked up as described in the oxidation of emetine by permanganate (Carr and Pyman, *loc. cit.*, p. 1630), the only crystalline product obtained was 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid (yield 0·16 g.), which was recognised by its appearance, content of water of crystallisation (Found: loss at 100°, 13·9. Calc., 13·4%), and behaviour on heating, the dried substance melting from 204° to 209° (corr.) according to the rate of heating, effervescing, and leaving an alkaline residue.

(2) *By chromic acid.* On adding aqueous chromic acid in excess to a warm aqueous solution of *O*-methylpsychotrine sulphate, a brown, gummy precipitate was obtained which became a bright yellow, crystalline powder on rubbing (Found, in substance dried at 100°: Cr, 13·9. $C_{29}H_{38}O_4N_2,H_2Cr_2O_7$ requires Cr, 14·9%). It was almost insoluble in water. This salt (1·6 g.) was suspended in water at 100° for 60 hours, the volume being kept at 60—70 c.c. The product was mixed with sodium hydroxide, extracted with ether (E), and filtered. The filtrate was acidified with hydrochloric acid, and extracted with chloroform, which left 0·25 g. of residue on distillation. A hot aqueous extract of this residue deposited rubremetine hydrochloride, recognised by its characteristic appearance and m. p. (air-dried, 125°; dried at 100°, from 160°). The ethereal extract (E) gave crude *O*-methylpsychotrine (0·45 g.), yielding 0·35 g. of the crystalline hydrogen oxalate from which the pure base (m. p. 123—124°) was readily obtained.

Partial Demethylation of O-Methylpsychotrine.—Methylpsychotrine sulphate heptahydrate (10 g.) and hydrochloric acid (1·54 c.c.; 34%) were heated for 6 hours at 170°. The product was dissolved in water (50 c.c.) and shaken with ether, and excess of ammonia was added gradually; psychotrine (3·0 g.) then crystallised. This was dissolved in alcohol and mixed with an alcoholic solution of oxalic acid (1·5 g.); psychotrine hydrogen oxalate (3·2 g.) then separated (mother-liquor M). The filtrate from the psychotrine was separated into ethereal and aqueous layers and the former was extracted with aqueous sodium hydroxide (ethereal solution E). This was mixed with excess of ammonium chloride, combined with the aqueous layer and extracted with chloroform; the extract then gave with alcoholic oxalic acid more psychotrine hydrogen oxalate (2·1 g.). The mother-liquor from this and the mother-liquor M gave, after further similar treatment, another small crop (0·25 g.) of the same salt. The residue from the ethereal solution E gave, with alcoholic oxalic acid, methylpsychotrine hydrogen oxalate (2·4 g.).

The yields in this experiment and others in which the period and temperature of heating were varied appear below:

Time (hrs.).	Temp.	% Yield of psychotrine.	% Methylpsychotrine recovered.
3	150°	8	74
6	150	12	71
3	170	37	50
6	170	54	23

The psychotrine obtained by demethylation of methylpsychotrine was identical with the natural alkaloid. The bases from each source and mixtures of the two sintered from 115° and melted and effervesced at 122° (corr.), when air-dried, and softened from 122° and melted and effervesced at about 129° (corr.), after drying in a vacuum over sulphuric acid. Psychotrine from its methyl ether, like the natural base, crystallised from aqueous acetone in well-formed, yellow prisms containing $4H_2O$ (Found: H_2O, 13·3. Calc.: H_2O, 13·4%). Crystals from each source were found to be identical crystallographically by Mr. G. Greenwood, M.Sc., of the University of Manchester, to whom the authors are much indebted for his examination and for the following data:

Crystal system: orthorhombic. $a : b : c = 0{\cdot}989 : 1 : 1{\cdot}209$.
Forms observed: {100} {010} {110} + {101}.

Angle measured.	Natural psychotrine (obs.).	Psychotrine from its methyl ether (obs.).	Calc.
(100) : (101)	39° 20′	39° 18′	—
(110) : (101)	56° 35′	56° 41′	—
(100) : (110)	44° 38′	44° 50′	44° 41′

Mr. Greenwood adds: "It is interesting that the ratio *a* : *b* is so near to 1 : 1 and the angle (100) : (110) to 45°. If this were actually the case, the crystal would be tetragonal. I am afraid the angle measurements were really not good enough to settle this point. Also the crystals were too poor to examine the optical properties, which would again have decided this question. However, judging from the geometrical properties of the faces on the ends of the crystals, I think that there is no doubt that the crystals are not tetragonal and that the equality of *a* and *b* is merely a chance effect."

Psychotrine hydrogen oxalate readily separates in nearly colourless needles when alcoholic solutions of its constituents are mixed. It is very sparingly soluble in alcohol, but readily soluble in water. After drying in a vacuum over sulphuric acid, it softens from 130° and melts and effervesces up to 145° (corr.) [Found, (*a*) in salt crystallised from water, (*b*) in salt from alcohol: loss in vacuum over H_2SO_4, (*a*) 10·3; (*b*) 9·0. $C_{28}H_{36}O_4N_2,2C_2H_2O_4,4\frac{1}{2}H_2O$ requires loss of $4H_2O$, 10·0%. Found in dried salt: C, 58·7, 58·6; H, 6·6, 6·6. $C_{28}H_{36}O_4N_2,2C_2H_2O_4,\frac{1}{2}H_2O$ requires C, 58·8; H, 6·3%].

Emetamine.

Purification of Emetamine.—111 G. of emetamine hydrogen oxalate having $[\alpha]_D - 5°$, prepared by the method described earlier (Pyman, Part II, *loc. cit.*), were subjected to further fractionation as follows. The base was regenerated in chloroform by means of sodium hydroxide, and extracted six times with sufficient 2% sulphuric acid to remove 5% of the base at each extraction. Each extract and the mother-liquor were then basified, and the extracted bases were converted separately into the hydrogen oxalates. The yields and specific rotatory powers (of air-dried salt in water; $c = 4$) were as follows: (1) 4·6 g. (coloured); (2) 5·2 g., $[\alpha]_D - 4·7°$; (3) 5·0 g., $[\alpha]_D - 5·7°$; (4) 4·6 g., $[\alpha]_D - 6·2°$; (5) 5·0 g., $[\alpha]_D - 6·0°$; (6) 5·2 g., $[\alpha]_D - 6·4°$; remainder 55·7 g., $[\alpha]_D - 6·3°$. The last fraction, which was regarded as pure, was converted into the base, and through this into other salts. Its specific rotatory power is in close agreement with that previously recorded ($[\alpha]_D - 6·0°$).

Emetamine.—When emetamine is regenerated, in chloroform, from a salt and crystallised from ethyl acetate, it is free from solvent and melts at 153—154° (corr.) [Pyman, *loc. cit.*, gives 155—156° (corr.)], but when it is regenerated in ether, the ethereal solution, after being dried for a few minutes over potassium carbonate and filtered, deposits emetamine in colourless needles containing solvent of crystallisation. In this form, the air-dried base has m. p. 138—139° (corr.), and $[\alpha]_D + 13·6°$ in commercial absolute alcohol ($c = 2·2$); after drying in a vacuum at 100°, the base has m. p. 142—143° (corr.). It appears to contain $\frac{1}{2}$ mol. of ether of crystallisation [Found, in air-dried base: loss at 100° in a vacuum, 7·1; loss over in water (50 c.c.) and shaken with ether, and excess of ammonia was added gradually; psychotrine (3·0 g.) then crystallised. This was dissolved in alcohol and mixed with an alcoholic solution of oxalic acid (1·5 g.); psychotrine hydrogen oxalate (3·2 g.) then separated (mother-liquor M). The filtrate from the psychotrine was separated into ethereal and aqueous layers and the former was extracted with aqueous sodium hydroxide (ethereal solution E). This was mixed with excess of ammonium chloride, combined with the aqueous layer and extracted with chloroform; the extract then gave with alcoholic oxalic acid more psychotrine hydrogen oxalate (2·1 g.). The mother-liquor from this and the mother-liquor M gave, after further similar treatment, another small crop (0·25 g.) of the same salt. The residue from the ethereal solution E gave, with alcoholic oxalic acid, methylpsychotrine hydrogen oxalate (2·4 g.).

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Mr. Greenwood adds: " It is interesting that the ratio $a : b$ is so near to 1 : 1 and the angle (100) : (110) to 45°. If this were actually the case, the crystal would be tetragonal. I am afraid the

Attempts to prepare emetamine acetate, salicylate, sulphate, and tartrate in crystalline form were unsuccessful.

Emetamine dimethiodide was prepared by heating the base with methyl iodide for 7 hours at 100°. It crystallised from aqueous alcohol in prismatic needles, which began to effervesce at 238° (corr.) (Found, in air-dried salt: loss at 110°, 2·2. $C_{31}H_{42}O_4N_2I_2,H_2O$ requires H_2O, 2·3%. Found, in dried salt: I, 33·0. $C_{31}H_{42}O_4N_2I_2$ requires I, 33·4%).

Action of Bromine upon Emetamine.—The base from emetamine hydrogen oxalate (1·8 g.) in chloroform (30 c.c.) was mixed with bromine (0·25 c.c.) in chloroform (10 c.c.). After 5 minutes, the solution was shaken with ammonia and dried with potassium carbonate, and the solvent was removed. The residue was extracted with boiling water, and the extract concentrated; it then deposited less than 0·1 g. of a red, microcrystalline substance, resembling rubremetine hydrobromide in colour and sparing solubility in water, but melting, when air-dried, at 185—190°. (Air-dried rubremetine hydrobromide melts at about 115—120°.) The material insoluble in hot water was dissolved in dilute hydrochloric acid, and the bases were liberated by ammonia in the presence of ether, a considerable amount of dark brown resinous material being precipitated; the ethereal solution gave a residue (0·3 g.), from which emetamine hydrogen oxalate (0·25 g.; m. p. 165—170°) was prepared.

Reduction of Emetamine.—(a) *With sodium and alcohol.* In view of the importance attaching to the formation of benzoyl*iso*emetine from emetamine (Part II, p. 443), the reduction of emetamine with sodium and alcohol was repeated, the specially purified emetamine described above being used, and the formation of *iso*emetine was confirmed by the isolation of its benzoyl derivative.

(b) *With tin and hydrochloric acid.* The reduction of emetamine by this means proceeds very slowly, and in the following experiment much emetamine was recovered unchanged, but again benzoyl*iso*emetine was readily obtained from the reduced portion.

The base regenerated from emetamine hydrogen oxalate (3·55 g.) was heated with alcohol (20 c.c.), concentrated hydrochloric acid (20 c.c.), and tinfoil (8 g.) for 13 hours under reflux. The base (1·3 g.), regenerated in ether, was converted into hydrogen oxalate in alcohol; crude emetamine hydrogen oxalate (1·1 g.) then crystallised. The base (0·4 g.) regenerated from the mother-liquor was mixed with benzoic anhydride (0·4 g.) in dry ether; the deposited benzoyl*iso*emetine (0·08 g.), after being washed with acetone, melted at 207° (corr.), alone or mixed with a known specimen of benzoyl*iso*emetine.

The authors desire to thank Professor Robert Robinson, F.R.S., for the very considerable help which he has given them by suggestion and discussion in determining the constitution of the alkaloids of ipecacuanha, and to thank Mr. J. A. Goodson, F.I.C., for assistance in the earlier stages of the separation of emetamine from *O*-methylpsychotrine.

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[*Received, April 7th*, 1927.]

CXLV.—*The Periodic Electro-deposition of Metals through Secondary Reaction.*

By ERNEST SYDNEY HEDGES.

EXPERIMENTS described in a series of papers by the present author (J., 1926, 1533, 2580, 2878) have shown that periodic changes in current density and potential occur in the electrolytic dissolution of a number of metals in various electrolytes. The present communication contains an account of the inversion of this process—the periodic deposition of a metal at the cathode.

The method of investigation was essentially similar to that in the experiments on the anode (*loc. cit.*) but certain important improvements were made: Instead of measuring the total *P.D.* across the electrolytic cell, the *P.D.* between the cathode alone and a standard reference electrode was determined. Also, the measurements were made by a static instrument, so that absolutely no current was taken from the system. Since it was anticipated that rapid alterations of potential would have to be followed, a string electrometer was used as the measuring instrument. This has the advantage that it is entirely dead-beat, and can therefore be used for following very rapid vibrations, and its sensitivity is adjustable over a wide range.

The same electrolysis vessel was used as before, but it was now provided with a side-tube leading to a bridge of *N*-potassium chloride, making connexion with a *N*-potassium chloride calomel half-element. The cathode was connected to the string of the electrometer and the calomel cell was earthed. During electrolysis, the *C.D.* was progressively raised and the position of the fibre was noted on the scale in the eye-piece, the scale being adjusted so that 25 divisions corresponded to 1 volt. All the experiments were conducted at 30° and a platinum anode was used throughout.

Periods in Direct Deposition.

The conditions of the first experiments were designed to be as nearly as possible analogous to those known to be favourable to periodicity at the anode. Thus, attempts were directed towards depositing a metal in presence of an acid which would dissolve it, in the anticipation of reaching a boundary state where a deposit of metal would form and dissolve off alternately. Experiments of this type on the deposition of iron and of zinc from various solutions of their salts in presence of acids met with no result.

It was hoped to realise a periodic deposition of alkali metals in the electrolysis of solutions of their salts with a mercury cathode, for here there is a possibility of a balance between the rate of deposition of the metal and the rate of dissolution by the water. Experiments with $2N$-, N-, and $N/10$-solutions of alkali salts were unsuccessful. However, it seems that at these concentrations the sodium dissolves off the cathode too easily, for later experiments have shown that periods can be realised in the electrolysis of $4N$-caustic soda with a mercury cathode.

Actually, periods were observed by Coehn (*Z. Elektrochem.*, 1901, 7, 633) in the electrolysis of caustic soda with a mercury cathode, although experimental details are not given. The experiment was repeated by Kremann and Lorbeer (*Sitzungsber. Akad. Wiss. Wien,* April, 1913) using $3N$-caustic soda. The present author has confirmed these results and finds that the phenomenon is readily reproduced at 30° with $4N$-caustic soda, at a *C.D.* of 300 milliamp./cm.^{2}. Alternate periods of amalgam formation and dissolution took place, the periods becoming longer with time. The electrical change was very slight, the cathode *P.D.* being $-$ 2·08 volts during amalgam formation and $-$ 2·00 volts during dissolution of the amalgam.

There seems little doubt that the periods mentioned by Förster (*Z. Elektrochem.*, 1902, 8, 500) in the deposition of copper from a nitric acid solution of the nitrate, and by Coehn (*ibid.*, p. 499) in electrolysing a solution of nitric acid in which bismuth had been dissolved, were due to a similar cause. The phenomenon mentioned by the present author (J., 1926, 1543) concerning a copper anode in nitric acid was probably due to periodicity at the cathode, where deposition of copper took place.

During the experiments on film formation at an unattackable anode (J., 1926, 2591), it was sought to deposit mercuric cyanide and cadmium cyanide, respectively, at the anode by electrolysing solutions of potassium mercuric cyanide or potassium cadmium cyanide; although this deposition did not occur, yet in both cases, between certain current densities, a periodically fluctuating potential appeared, which had its source in the *cathode*, at which a periodic evolution of hydrogen bubbles was visible. The interpretation then placed on the phenomenon was that at the cathode, which had now become mercury (or cadmium) by deposition, potassium ions were discharged and periodically reacted with the solution giving hydrogen. In fact, this led to the experiments described above with alkali-metal salts.

Since the experiments on the deposition of sodium and potassium at similar concentrations at a mercury cathode gave negative results, attention was directed to the simultaneous deposition of mercury and potassium at a platinum cathode.

Experiments on the Simultaneous Deposition of Metals.

Preliminary experiments showed that a *N*/10-solution of mercuric chloride was almost non-conducting, and the small amount of product formed at the cathode appeared to be calomel. This is not surprising since, according to Luther (*Z. physikal. Chem.*, 1901, **36**, 402), a solution of mercuric chloride saturated at 25° contains $1{\cdot}5 \times 10^{-4}$ mol. per litre of the $HgCl^{\cdot}$ ion and only 10^{-8} of the $Hg^{\cdot\cdot}$ ion. It was found, however, that deposits of mercury were readily formed when the solution also contained *N*/10-potassium chloride or *N*/10-hydrochloric acid. It may be noted that, since the solution contains practically no mercuric ions, the mercury is deposited through a secondary reaction, *i.e.*, either potassium or hydrogen is discharged first and reacts with the complex $HgCl_4''$ ion, and perhaps with undissociated $HgCl_2$.

The Deposition of Potassium with Mercury.—Periods were first observed in the electrolysis of a solution containing *N*/10-mercuric chloride and *N*/10-potassium chloride, using a *C.D.* of 16 milliamp./cm.^{2}. The cathode potential then oscillated between − 1·6 and − 2·0 volts in periods of 1 minute. (Normal calomel electrode taken as zero.) In these experiments, two platinum electrodes, each of 12 sq. cm. available area, were used, although the cathode necessarily soon became a mercury electrode. Periods were obtained under similar conditions when an electrode of pure mercury was used, but it seemed better for practical reasons to use a cathode of platinum and allow the deposited metal to form a coating thereon.

It was evident that these periods required the simultaneous deposition of two metals, for when such a system was oscillating the electrodes were removed and placed in *N*/10-potassium chloride and *N*/10-mercuric chloride separately. No periods could be obtained in either solution, but when the electrodes were put back into the original solution of the mixed substances the periods continued.

At first, certain difficulties were encountered in the reproduction of these results, and these were traced to the fact that during electrolysis the ratio of mercury to potassium in the solution continuously diminishes; for ultimately the mercury is entirely deposited, whilst the potassium content of the solution remains unaltered. One source of difficulty was that at the commencement of the electrolysis, when the solution was rich in mercuric chloride, a film of mercurous chloride tended to form on the cathode. This could be loosened and thrown off the cathode by breaking and making the circuit several times in succession, or by increasing the cathode potential to the point of incipient hydrogen evolution.

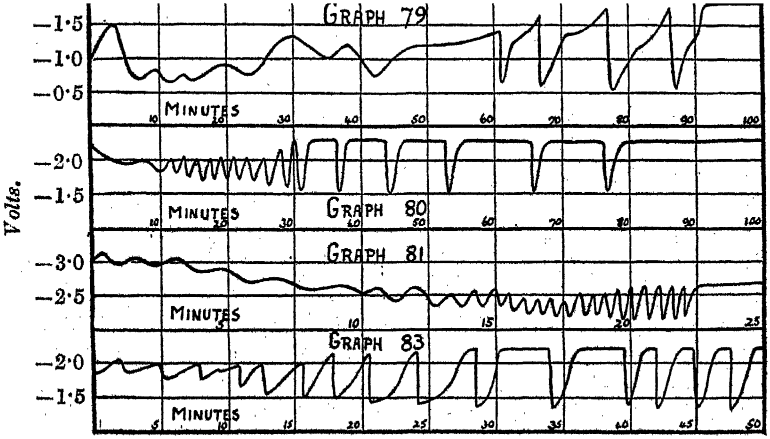
A second inconsistency was that the conditions of formation of the periods appeared to differ in each experiment and did not correspond with any definite values of *C.D.* and potential. The general relations were these: below a certain critical *C.D.* mercury was deposited; above a higher critical *C.D.* hydrogen was evolved (potassium ions discharged); between these limits the electrode oscillated from one state to the other in regular periods. But the limits of the region of periodicity varied continuously throughout the course of the electrolysis. This was traced to the change in the concentration of the mercuric chloride, and it appeared that the critical limits of *C.D.* were lower the greater the ratio of potassium to mercury in the solution. Thus, a mixture consisting of *N*/40-mercuric chloride and *N*/10-potassium chloride gave a continuous evolution of hydrogen at the lowest *C.D.*'s, whilst a mixture consisting of *N*/5-mercuric chloride and *N*/10-potassium chloride required initially a high *C.D.* in order to reach the lower limit of the region of periodicity, although this critical *C.D.* fell continuously as the solution became weaker in mercuric chloride.

The use of a mercury anode would *increase* the concentration of mercury continuously, even if it were permissible in a chloride solution. The composition of the solution could be kept constant by employing a saturated solution of mercuric chloride in potassium chloride in presence of excess of solid mercuric chloride. Although this has not been done in the system under discussion, it has been done in other systems, and the resulting waves have been regular and continuous.

The most favourable mixtures were solutions containing *N*/10- or *N*/20-mercuric chloride and *N*/10-potassium chloride, and the method devised for securing comparable conditions was to electrolyse with a constant *C.D.* of 42 milliamp./cm.^{2}. This was below the critical *C.D.* required at the commencement of the electrolysis, but, owing to the gradual deposition of the mercury, after a time the solution reached a composition such that this *C.D.* produced periods, and finally the *C.D.* employed corresponded to the upper limiting value for the solution, causing steady evolution of hydrogen.

Thus, for a given composition of solution there exists a current density-region of periodicity, and for a given *C.D.* there is a composition-region of periodicity. The latter is illustrated by Graphs 79 and 80, showing the transition of the electrode from the state of mercury deposition, through the region of periodicity, and into the state of continuous hydrogen evolution. Graph 79 represents the change with time of the cathode potential in the electrolysis of a mixture containing *N*/20-mercuric chloride and *N*/10-potassium chloride, using a *C.D.* of 9 milliamp./cm.^{2}. Graph 80 similarly represents the electrolysis of *N*/10-mercuric chloride and *N*/10-potassium chloride with a *C.D.* of 42 milliamp./cm.^{2}. The periods have an amplitude of about 0·8 volt. At the more negative values of potential very strong evolution of hydrogen occurred in the form of small bubbles and the surface was dull through the formation of potassium amalgam, whilst at the less negative values the mercury was bright and only a few large bubbles of hydrogen adhered to it.

Fig. 1.



Deposition of other Metals with Mercury.—Similar periods were obtained in the simultaneous deposition of sodium and mercury. Graph 81 records the variation of the cathodic potential with time in the electrolysis of a solution containing *N*/10-mercuric chloride and *N*/10-sodium sulphate with a *C.D.* of 42 milliamp./cm.^{2}. During the first stage of the reaction, mercury was deposited and the electrode became covered with a few large bubbles of hydrogen. In the second, oscillatory stage, violent evolution of hydrogen in the form of small bubbles occurred at regular intervals, whilst after 22 minutes steady hydrogen evolution set in. The initial fall of *P.D.* is due to the gradual increase in conductivity of the solution due to the liberated chlorine ions from the complex anions. The periods were fairly rapid, having an interval of 30 seconds.

Equally good periods were obtained in the electrolysis of a solution of *N*/10-mercurous nitrate and *N*/10-sodium nitrate.

A solution of *N*/10-mercuric chloride and *N*/10-barium chloride electrolysed with a *C.D.* of 4 milliamp./cm.^{2} gave excellent periods, the cathode *P.D.* changing from $-$ 0·8 to $-$ 1·8 volts every 30 seconds. Similarly, with a solution containing *N*/10-mercuric chloride and *N*/10-strontium chloride the *P.D.* oscillated between $-$ 1·7 and $-$ 2·4 volts in 2-minute periods, using a *C.D.* of 42 milliamp./cm.^{2}. Graph 83, which was obtained with *N*/10-mercuric chloride and *N*/10-calcium chloride under the same *C.D.*, is typical of the results obtained with these mixtures.

Periods were also obtained in the electrolysis of a solution of *N*/10-mercuric chloride and *N*/10-aluminium sulphate. These were somewhat irregular, but had an average interval of 2 minutes and an amplitude of about 0·4 volt.

Periods were not observed under any conditions in the electrolysis of solutions containing *N*/10-mercuric chloride with an *N*/10-solution of magnesium, zinc, copper, or nickel sulphate.

It was of interest to determine whether positive amalgam formation was necessary for the production of periods, or whether the direct discharge of hydrogen could produce a similar effect, and therefore the electrolysis of a solution containing *N*/10-mercuric chloride and *N*/10-hydrochloric acid was investigated. When hydrogen evolution started, however, the gas left the cathode in the form of very large bubbles, so that a constant *P.D.* could not be obtained and it was not possible to decide the point. Similar experiments at a cadmium cathode (*vide infra*), however, show that in this case hydrogen cannot act in such a way.

Deposition of Metals with Cadmium.—The salts of cadmium resemble those of mercury in their tendency to complex formation, and it is not surprising, therefore, to find a similar behaviour in the simultaneous deposition of cadmium and sodium. A solution containing *N*/5-cadmium nitrate and *N*/10-sodium sulphate gave at low *C.D.*'s a deposit of cadmium on the cathode, whilst at high *C.D.*'s a gelatinous film of cadmium hydroxide formed round the cathode and hydrogen was evolved. Intermediate *C.D.*'s covered a wide region in which the film of cadmium hydroxide formed periodically, whilst the cathode *P.D.* oscillated regularly between $-$ 2·25 and − 2·4 volts; in these periods it was at the higher negative value while the film was on the electrode and hydrogen was being evolved, and at the lower potential the film as a whole slipped off the cathode, and metallic cadmium was deposited.

The following table shows that the frequency of these periods increases rapidly with increase of *C.D.* (The reverse was found to hold for the anodic periods, *q.v.*)

Milliamp./cm.^{2}	13	15	17	25	33	42	58
Period (secs.)	26	19	14	7	5	3	2

The only difference between these periods and those with mercury is that cadmium hydroxide is formed at the cathode in place of metallic mercury. This is due to the relative ease with which the oxide of mercury is reduced.

As it is not necessary further to multiply instances, experiments have not been conducted with other alkali metals and cadmium, although there is every reason to suppose that they would behave similarly. It was of interest, however, to examine the effect of hydrogen itself, and solutions containing *N*/5-cadmium nitrate and *N*/2-, *N*/5-, and *N*/10-sulphuric acid, respectively, were electrolysed. No periods were observed.

Deposition of other Metals with Alkali Metals.—Electrolysis of solutions of zinc sulphate with sodium sulphate gave no periods, and negative results were likewise obtained in electrolysing mixtures of copper sulphate with sodium sulphate, and silver nitrate with sodium nitrate. In these cases the metals are deposited directly and not by secondary reaction.

Electrolysis of Cyanide Solutions.—Double cyanides on electrolysis furnish excellent examples of the deposition of a metal through a secondary reaction, and therefore promised to be a fruitful ground for the study of periodicity of the type under discussion. The extreme regularity of the periods is a feature of these experiments, enabling these systems to be used for a quantitative examination.

Mercury potassium cyanide. Mercuric chloride solution was added to 50 c.c. of *N*/2-potassium cyanide until a permanent precipitate was formed, and the solution was then made up to 100 c.c. Electrolysing with a *C.D.* of 9 milliamp./cm.^{2}, excellent periods were obtained from this system, though the amplitude was on the whole considerably less than in the foregoing cases.

The following table shows how, in such an experiment, the amplitude increases to a maximum and then declines, whilst the frequency simultaneously increases (period decreases) and then falls off. It will also be observed that the product of amplitude and period is as constant as could be expected.

Time (mins.).	Amplitude (volts).	Period (secs.).	Product.
0	0·2	0·4	0·08
3	0·3	0·29	0·087
6	0·35	0·24	0·082
9	0·4	0·20	0·080
12	0·4	0·24	0·096
17	0·4	0·19	0·076
24	0·35	0·20	0·070
30	0·3	irreg.	?
34	0·3	0·31	0·093
36	0·25	0·42	0·105
38	0·2	0·5	0·100
40	0·1	1·1	0·110
42	0·0	∞	—

In this system, the frequency decreases greatly with increasing *C.D.*, as shown by the following table :

Milliamp./cm.^{2}	6·2	8·3	9·2	10·0	12·5	17·7
Period (sec.)	*ca.* 0·1	0·2	1·1	5·0	13·0	∞

The frequency was measured by taking the time for 10 successive periods with the aid of a stop-watch. Experience showed that it was possible faithfully to count periods at the rate of 6 per second, although values for higher frequencies were not trustworthy. At the *C.D.* of 6 milliamp./cm.^{2}, the period was judged to be about 0·1 sec. because the movement of the electrometer fibre, as judged by the eye, bordered on to continuity. At a slightly lower *C.D.*, the period was almost certainly rather less than this value.

Taking 0·1 sec. as the smallest duration of a period that has been observed, however, it becomes of interest to calculate the thickness of the film of mercury deposited during that period. Thus, a current of 6·2 milliamp. deposits during 0·05 sec. (mercury is deposited only during each half-period) $3{\cdot}24 \times 10^{-7}$ g. of mercury on an area of 1 cm.^{2}. Assuming that the mercury has its normal density of 13·6, the thickness of the mercury film deposited in each period is $2{\cdot}4 \times 10^{-8}$ cm., *i.e.*, of the order of molecular thickness.

No significance is to be attached to this result in the theory of the subject, for it can be shown that in other cases the thickness of the film formed in each period corresponds to several thousands of molecules; but the important point is that *we have here a case of periodicity in the smallest amount of chemical change.*

At these low *C.D.*'s the amount of chemical change was not sufficient to produce visible periodic evolution of hydrogen, but, nevertheless, the periodicity was easily visible, for the hydrogen bubbles, with which the surface of the cathode became covered, pulsated synchronously with the periodic change of potential. This effect, due to the periodically changing surface tension at the mercury–hydrogen interface as a result of the periodic formation of amalgam, showed itself in a pulsating flattening of the bubbles. The effect was perceptible when the amount of metal deposited in each pulsation could not have exceeded a few molecules in thickness.

Cadmium potassium cyanide. Even better periods were obtained with a solution made by adding cadmium nitrate to 50 c.c. of *N*/2-potassium cyanide until a permanent precipitate formed, and then making up to 100 c.c. These differed from the periods last mentioned in that considerably higher *C.D.*'s could be used, the amplitude was larger (generally about 0·5 volt), and the frequency *increased* with rise of *C.D.* It is noteworthy that in cyanide solutions the frequency is always high.

The next table shows the change in frequency with increase of *C.D.* In the third column appear values of *K*, the product of the square of the current into the period, and it will be seen that over a wide range these are remarkably constant, considering the error in measuring such small periods.

Total current (milliamp.).	Period (secs.).	*K*.	Total current (milliamp.).	Period (secs.).	*K*.
0·25	2·0	0·125	0·55	0·32	0·097
0·30	0·9	0·082	0·60	0·22	0·080
0·35	0·8	0·098	0·65	0·18	0·076
0·40	0·6	0·096	0·75—1·75	very rapid	—
0·45	0·5	0·101	1·9	0·00	—
0·50	0·4	0·100			

In this case then, the period is inversely proportional to the square of the *C.D.* In this experiment, excess of cadmium cyanide was added so that the composition of the solution should not change during electrolysis. Similar results were obtained whether a cadmium or a platinum cathode was used. Pulsating evolution of hydrogen was visible.

Electrolysis of other Systems.—Periods could not be obtained at the cathode in the electrolysis of solutions of the double cyanides of potassium with copper, silver, iron, nickel, cobalt, and zinc. With the exception of zinc, the hydrogen overvoltage is low, and therefore hydrogen was liberated simultaneously with the metal at all *C.D.*'s, and the zinc potassium cyanide solutions were hydrolysed too readily. Unsuccessful experiments were also carried out with solutions of zinc hydroxide and of lead hydroxide in caustic soda. Poor periods were obtained, however, in the deposition of tin from a solution prepared by adding excess of caustic soda to 25 c.c. of *N*/2-stannous chloride and then making up the volume to 100 c.c. The cathode potential varied between $-1{\cdot}36$ and $-1{\cdot}48$ volts in slow periods of 15 minutes, using a *C.D.* of 7 milliamp./cm.^{2}.

Discussion.

The mechanism of the periodicity will be considered for the typical case of the electrolysis of cadmium potassium cyanide solutions. At low *C.D.*'s potassium ions are discharged, and react with the complex $\mathrm{Cd(CN)}_4''$ ions: cadmium is deposited and no hydrogen appears. But at a certain critical *C.D.* more potassium ions are discharged than can react with the complex ions, so the excess react with the water molecules and hydrogen is evolved. It is evident that the liberated potassium ions dispose of the complex $Cd(CN)_4''$ ions preferentially, and only react with water when these become scarce.

The surprising feature is that after a short interval of time the discharged potassium ions cease to react with water, and again are entirely concerned with the complex ions of cadmium.

This point touches the fundamental question of the cause of periodicity, to which an answer cannot at present be given, research so far having been directed towards discovering the conditions under which periodicity is manifested. A discontinuity must occur at some stage in the mechanism of the reaction. In the experiments on the anode there was some evidence to show that the film as first deposited was unstable and changed suddenly to a stable state. This may also be the case here, although it may be pointed out that the phenomenon is equally explicable on the assumption that a certain critical concentration of the complex ions in the immediate vicinity of the cathode is necessary before reaction takes place.

Whether this be the case or not, it is tolerably certain that the discharged potassium ions react alternately with the complex cadmium anions and with the water molecules. The variation of the period with the inverse square of the *C.D.* finds a ready explanation when one considers the relations in the layer of solution immediately contiguous to the cathode; for, suppose the *C.D.* to be increased n times: then the rate of discharge of potassium ions is increased n times, and the rate of migration of the complex anions from the immediate vicinity of the cathode is increased n times. Since there are n times as many potassium ions discharged, and $1/n$ of the number of $Cd(CN)_4''$ ions to react with, the latter become used up n^2 times as quickly.

It is to be remembered, however, that in the electrolysis of mercury potassium cyanide solutions the period *increased* with rise of *C.D.*; but another factor enters here, for whereas with cadmium potassium cyanide the discharged potassium ion is confronted with the alternatives of reacting with the complex anions or with water molecules, yet another possibility is open in the case of mercury potassium cyanide in that the potassium atom may stay as such in the mercury. Moreover, increase of *C.D.* will stabilise the potassium amalgam, diminishing its tendency to react.

The present work shows that a satisfactory explanation of periodic phenomena in electrolysis must be founded upon as wide a basis as possible in order to include both anodic and cathodic reactions and the discharge of one or more ions. Elsewhere (Hedges and Myers, "The Problem of Physico-chemical Periodicity," Arnold and Co., 1926) the author has gathered together some reports of earlier experiments of this type. Since these are mostly isolated cases, the earlier investigators proposed a specific mechanism for each. It is now evident that an explanation should be of general applicability. It is hoped by further experiment to eliminate some of the factors which at present lead to ambiguity in interpretation.

Summary.

Periodic changes in the cathode potential and current strength occur between certain limiting current densities during the electrolysis of solutions composed of a mixture of mercuric chloride or mercurous nitrate with solutions of the salts of alkali metals, alkaline earths, or aluminium, and in solutions of mercuric cyanide or cadmium cyanide in potassium cyanide. The phenomenon consists of the alternate deposition of two metals, and has been observed only when one of the metals is deposited through a secondary reaction. The values of the limiting current densities, between which the region of periodicity exists, depend on the relative amounts of the components of the mixed solution. Periodicity has been realised where the amount of metal deposited in each period does not exceed a few molecules in thickness.

The author is indebted to Dr. J. F. Spencer for his interest in this work, and to the Research Fund Committee of the Chemical Society and the Trustees of the Dixon Fund of the University of London for grants which have assisted its prosecution.

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CXLVI.—*Molybdenyl Salts and the Co-ordination Number of Oxygen.*

By WILLIAM WARDLAW and ROBERT LOUIS WORMELL.

ACCORDING to the acid concentration, red or green solutions containing tervalent molybdenum are produced by the electrolytic reduction of molybdenum trioxide in hydrochloric acid. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173) suggested that the appearance of the green colour might be due to the formation of small masses of molybdenum dichloride which had not been detected chemically, and that in the red solutions bivalent molybdenum was not produced. The existence of two differently coloured solutions of chromic chloride is well known. Peligot (*Compt. rend.*, 1844, **19**, 783; *Ann. Chim. Phys.*, 1844, **12**, 537) first succeeded in obtaining green crystals of chromium trichloride, $[\mathrm{Cr(H_2O)_4Cl_2]Cl,2H_2O}$, by treating the insoluble violet anhydrous trichloride with water in the presence of a small quantity of chromium dichloride. Attempts to isolate isomeric trichlorides of molybdenum have so far been unsuccessful, however.

Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458) conclude from their measurements of potential, that the existence of bivalent molybdenum in the green solutions is highly improbable. In view of the isolation of the complex salts $\mathrm{R_3MoCl_6}$ and $\mathrm{R_2MoCl_5,H_2O}$ by the addition of alkali chlorides to solutions of tervalent molybdenum, these authors consider that the colours and properties of the green and red solutions may be due to the varying concentrations of the ions as determined by the equilibria:

$$[\mathrm{MoCl_6}]''' \rightleftharpoons \mathrm{Mo}^{\cdots} + 6\mathrm{Cl}'; \quad [\mathrm{MoCl_5,H_2O}]'' \rightleftharpoons \mathrm{Mo}^{\cdots} + 5\mathrm{Cl}' + \mathrm{H_2O};$$
$$[\mathrm{Mo,6H_2O}]^{\cdots} \rightleftharpoons \mathrm{Mo}^{\cdots} + 6\mathrm{H_2O}.$$

Nevertheless it is possible to obtain from a green solution of tervalent molybdenum the green oxychloride, $\mathrm{MoOCl,4H_2O}$, and from the red solution the brown isomeride, $\mathrm{MoOCl,4H_2O}$ (this vol., p. 130). These facts, together with the isolation of the salt $\mathrm{KMoOCl_2,3H_2O}$ (this vol., p. 512), furnish strong evidence in favour of the presence of the molybdenyl radical in all solutions of tervalent molybdenum, in accordance with the scheme

$$\mathrm{MoCl_3},x\mathrm{H_2O} \rightleftharpoons [\mathrm{MoOCl,4H_2O}] + 2\mathrm{HCl} + (x-5)\mathrm{H_2O};$$
$$[\mathrm{MoOCl,4H_2O}] + \mathrm{H_2O} \rightleftharpoons [\mathrm{MoO,5H_2O}]^{\cdot} + \mathrm{Cl}'.$$

Further proof of the existence of the molybdenyl radical is now received from the preparation of a series of its salts. In addition, the occurrence of a trichloride in the red solution, as postulated by Chilesotti, is confirmed by the isolation of the first *hydrated molybdenum trichloride*, the dark red crystalline substance $\mathrm{MoCl_3,3H_2O}$. Previously, the only known trichloride was the insoluble solid prepared by dry methods.

EXPERIMENTAL.

Preparation of Hydrated Molybdenum Trichloride.—A solution of molybdenum trioxide (10 g.) in 400 c.c. of hydrochloric acid (*d* 1·16) was heated on a water-bath for some hours, made up to 600 c.c., and electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 969) until the cathode solution was red. This solution was then evaporated to dryness at 70—80° under diminished pressure in an air-free flask. The residue was a copper-coloured, crystalline substance, which undoubtedly contained portions of hydrolysed material, and on analysis gave values of the order 1 : 2·5 for the ratio Mo : Cl. 400 C.c. of pure ether, cooled in a freezing mixture of ice and salt, and saturated with dry hydrogen chloride, were drawn into the flask by releasing the vacuum, and the red solution obtained was evaporated to dryness under diminished pressure, whereupon a dark red, crystalline substance separated. In order to ensure the complete conversion of any hydrolysed salt into the normal chloride, this operation was repeated. The substance finally obtained was quickly transferred in an atmosphere of dry carbon dioxide to a desiccator containing phosphoric oxide. The product was extremely hygroscopic, and exceptional precautions had to be taken to exclude moisture.

Analysis.—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The chloride in the filtrate and washings was estimated as silver chloride (Found : Mo, 36·44, 36·48; Cl, 40·77, 41·15; Mo : Cl = 1 : 3·03; 1 : 3·05. $MoCl_3,3H_2O$ requires Mo, 37·44; Cl, 41·49%).

Valency of the Compound.—This was determined as for the oxychloride (*loc. cit.*). One g. of the solid, on direct titration with standard permanganate, required 127·2 c.c. A similar solution, oxidised and passed through the reductor, required 130·2 c.c. The molybdenum is therefore tervalent.

Properties and Reactions of Molybdenum Trichloride.—The substance separates in dark, copper-coloured crystals, very soluble in water, acetone, or cold absolute alcohol, giving intensely red solutions. It rapidly reduces solutions of copper, silver, or mercuric salts. Sodium and ammonium hydroxides give black precipitates, soluble in acids; these are probably the trihydroxide. If potassium chloride is added to a solution of the substance in alcohol, the pink complex chloride, K_2MoCl_5,H_2O, is deposited on warming.

Salts containing the Molybdenyl Radical.—Molybdenyl bromide, like the chloride, has been obtained from a concentrated solution containing tervalent molybdenum by precipitation in acetone (J., 1926, 1592). Practical difficulties precluded the isolation of the corresponding fluoride in a similar way, but it has now been obtained by double decomposition of the oxychloride with ammonium fluoride in an air-free aqueous solution. *Molybdenyl fluoride* was deposited as a buff-coloured, insoluble precipitate the analysis of which agreed with the formula $MoOF,3{\cdot}5H_2O$. The properties of three out of the four possible molybdenyl halides of the general formula $[MoOR,4H_2O]$ can now be compared, and a close resemblance to the alkaline-earth halides is indicated inasmuch as the solubility of the molybdenyl halides increases with increase in the atomic weight of the halogen atom. Ease of hydrolysis accords with a similar generalisation.

Analysis of Molybdenyl Monofluoride.—The oxyfluoride, suspended in water, was brought into solution by the addition of sodium peroxide. In order to exclude ammonium salts, which have a solvent action on calcium fluoride, the alkaline solution was saturated with hydrogen sulphide, ruby-red thiomolybdate being formed. This was decomposed with dilute hydrochloric acid, and the precipitated sulphide was filtered off, ignited, and weighed as trioxide. The fluoride in the filtrate and washings was estimated as calcium fluoride (Found: Mo, 49·98, 49·60; F, 9·62, 9·45; Mo : F = 1 : 0·97, 1 : 0·96. $MoOF,3·5H_2O$ requires Mo, 49·49%).

The univalent molybdenyl radical, MoO, appears to persist in aqueous solution. The oxygen atom seems to be firmly attached to the molybdenum nucleus and the whole behaves like a univalent metal. This conception is supported by the existence of other insoluble molybdenyl salts, such as the benzoate, phosphate, salicylate (this vol., p. 130), and tartrate.

Preparation of Molybdenyl Derivatives.—By double decomposition of the theoretical amounts of molybdenyl monochloride and the alkali salts of benzoic, tartaric, and phosphoric acids, respectively, in air-free aqueous solution, reactions occur in accordance with the equations:

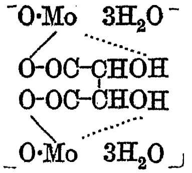
(1) $MoOCl + C_6H_5·CO_2Na = C_6H_5·CO_2·MoO + NaCl.$
(2) $2MoOCl + NaKC_4H_4O_6 = (MoO)_2C_4H_4O_6 + NaCl + KCl.$
(3) $3MoOCl + Na_2HPO_4 = (MoO)_3PO_4 + 2NaCl + HCl.$

These insoluble molybdenyl salts are all buff-coloured and undergo gradual hydrolysis in contact with water. They are best purified by washing with dilute solutions of the corresponding acids. Solutions of sodium oxalate and normal sodium citrate also give well-defined, buff precipitates when they are added to a solution of molybdenyl chloride. These precipitates are probably the corresponding molybdenyl salts.

Analysis. In the following analyses, the phosphate was estimated both as magnesium pyrophosphate and as ammonium phosphomolybdate. The percentages of water correspond to the whole of the hydrogen in the compound and not merely to that in the water of crystallisation. The benzoate was found to be tervalent by titration with permanganate solution. Found for $(MoO)_3PO_4,12H_2O$: Mo, 44·45; PO_4, 14·92. Calc.: Mo, 44·51; PO_4, 14·68%. Found for $C_6H_5·CO_2·MoO, 2·5H_2O$: Mo, 33·97; C, 29·95; H_2O, 31·75. Calc.; Mo, 34·53; C, 30·21; $5H_2O$, 32·39%. Found for

$(MoO)_2C_4H_4O_6,6H_2O$: Mo, 40·04; C, 9·96; H_2O, 29·65. Calc.: Mo, 40·00; C, 10·00; $8H_2O$, 30·00%.

These molybdenyl salts can be conveniently symbolised as co-ordination compounds in which the co-ordination number of tervalent molybdenum is six. On using such a formulation for the molybdenyl tartrate, it is seen that the tartrate grouping occupies four co-ordination positions :



The Co-ordination Number of Oxygen.

In dealing with the co-ordination number of multivalent atoms, Werner laid it down that oxygen and other bivalent atoms occupy only one position in the co-ordination sphere. Many examples could be quoted to support this view, but in other cases its acceptance involves assigning to an element an odd co-ordination number in circumstances which appear unlikely. Chromium, well known for the stability of its six-point system, forms salts of the type $[CrOCl_4]R$, in which, on Werner's view, the co-ordination number of chromium must be five. The same co-ordination number would be assigned to the central atom in the compounds $WOCl_4$, $MoOF_4$, $[VOF_4]K_2$, and $[NbOCl_4]C_5H_6N$. Nevertheless, the possibility that oxygen may occupy two positions, and thereby give rise to a co-ordination number of six, should not be overlooked. Electronic theories of valency have clearly demonstrated the essential difference between oxygen atoms occupying one or two positions in the co-ordination sphere. When an oxygen atom is attached to the central atom by a semipolar double bond, it occupies one co-ordination position, and when attached by a double bond, two. The resolution of the amine and phosphine oxides with the configuration $[R_1R_2R_3N \Rightarrow O]$ is explained most readily by supposing that the four units are tetrahedrally distributed round the central nitrogen or phosphorus atom, and that the oxygen bound to the central atom by a semipolar double bond occupies one position. Again, the optical activity associated with the sulphinates and sulphoxides (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, J., 1926, 2079) is satisfactorily explained by assigning to these substances a configuration $[O \Leftarrow SR_1R_2]$ in which the oxygen occupies one position in the tetrahedral structure.

Whilst the double link (two co-ordination positions) is required to avoid improbable co-ordination numbers in many compounds, such as those previously mentioned, it is especially necessary to explain the behaviour of carbon. If the carbonyl group were $\mathrm{C}\overset{\rightharpoonup}{=}\mathrm{O}$, the carbon would be tri-co-ordinated or tervalent. The results of Sugden and his colleagues (J., 1925, **127**, 1525) show, however, that carbon never forms a semipolar link with oxygen. This view is also supported by the conclusion from *X*-ray analysis, that the three oxygen atoms in the CO_3'' ion lie in the same plane with the carbon (W. L. Bragg, *Proc. Roy. Soc.*, 1914, *A*, **89**, 468), because with the tetrahedral model for carbon, the three atoms in $\mathrm{O{=}C{<}^{O}_{O}}$ would lie in a plane with the carbon, whereas in $\mathrm{O}\overset{\leftharpoonup}{=}\mathrm{C{<}^{O}_{O}}$ they would lie out of a plane as they do in $\mathrm{O}\overset{\leftharpoonup}{=}\mathrm{S{<}^{O}_{O}}$. On the basis of the *X*-ray result that the angle between the valencies to any two oxygen atoms in the CO_3'' and NO_3' ions is 120°, whereas that between the two singly-linked atoms might be expected to be 109° 28′, Lowry has assigned (*Chemistry and Industry*, 1927, 78) a trigonal orientation to the oxygen atoms around the central atom of the anion and concludes "that it is clear that van 't Hoff's tetrahedral model of the carbon atom now has a rival." It must, however, be borne in mind that "the tetrahedron representing a carbon atom is approximately regular only when the carbon atom is attached to four atoms of a similar kind" (Ingold, J., 1921, **119**, 306). Thus the tetrahedral angle must be modified in every case where the four linkings are not exactly equivalent, and on the Thorpe–Ingold theory this angle must be increased by the double link to the third oxygen. Moreover, since the two singly-linked oxygen atoms are negatively charged, they must repel each other and give rise to a greater value for the angle between them. It seems doubtful, therefore, whether any modification of van 't Hoff's conception is necessary or justified.

A suitable interpretation of the structure of those molybdenyl salts, such as $[\mathrm{MoOR},3{\cdot}5\mathrm{H_2O}]$, whose water content is less than would be anticipated from a co-ordination number of six for the molybdenum, would be to consider these compounds to be the result of the equilibrium

$$\mathrm{H_2O} + [\mathrm{MoOR},3\mathrm{H_2O}] = [\mathrm{MoOR},4\mathrm{H_2O}]$$

where, in one case, the oxygen occupies one position, and in the other, two positions in the co-ordination sphere.

The authors desire to thank the Chemical Society for a grant in aid of this investigation.

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[*Received, February 15th*, 1927.]

CXLVII.—*The Crystal Structure of Quinol. Part II.*

By William Augustus Caspari.

In a previous paper (J., 1926, 2944), some account was given of the *X*-ray examination of that trigonal modification of quinol which crystallises from aqueous solutions, and may be called α-quinol. There are, however, at least two other polymorphs, one of which, here referred to as γ-quinol, is monoclinic and has been known for a long time.

β-*Modification of Quinol.*—It was found in the course of the present investigation that when quinol is deposited from methyl-alcoholic solution at the ordinary temperature, it crystallises in hexagonal prisms resembling those of α-quinol at first sight, but belonging to a different subdivision of the trigonal system. This modification may be termed β-quinol. The crystals consist of prisms capped, not by rhombohedra, but by trigonal pyramids both of the first order, with a well-marked hemimorphism along the *c* axis. The typical crystal habit is shown in Fig. 1. In general, the crystals are not so excessively acicular as those of α-quinol, the prisms tending to be fairly thick in relation to their length. The density, 1·31, and m. p., 166°, are somewhat lower than those of α-quinol.

Fig. 1.

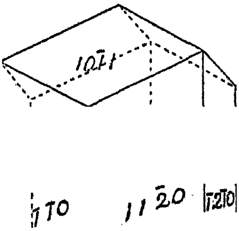
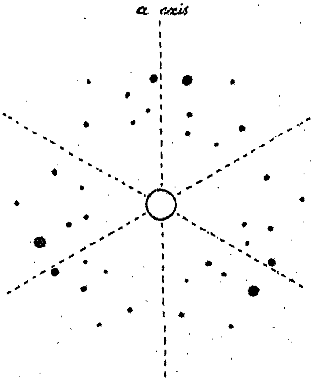


Fig. 2.



β-Quinol, Laue diagram through (0001), *as at distance* 1·75 *cm.*

From its external symmetry, β-quinol must be placed either in the ditrigonal-pyramidal (tourmaline) or in the trigonal-polar (sodium periodate) class. Definite evidence in favour of the latter class is afforded by Laue photographs through the (0001) plane. A diagrammatic reproduction, in which the size of the spots is an indication of their intensity, is given in Fig. 2. It will be observed that, whilst trigonal axial symmetry about c is well brought out, symmetry about planes parallel to c is absent. The latter planes being, apart from the triad axis, the characteristic symmetry elements of the tourmaline class, β-quinol can only possess the lower symmetry of the sodium periodate class, space-groups C_3^1 to C_3^4.

Under X-ray examination, the crystals reflect considerably better than those of α- or γ-quinol. Rotation photographs about axes normal to (0001), $(11\bar{2}0)$, and $(10\bar{1}0)$ gave the following results :

Cell-dimension c (mean of 7 spots on 2 layer-lines) : $c = 5{\cdot}53$ Å.
,, ,, a (,, 8 ,, 5 ,,) : $a = 16{\cdot}25$ Å.
,, ,, $a\sqrt{3}$ (,, 10 ,, 9 ,,) : $a\sqrt{3} = 28{\cdot}12$ Å.
whence $a = 16{\cdot}24$ Å.

In the c photograph the first layer-line is the strongest both in number and in intensity of spots. In all three photographs equally, $(30\bar{3}0)$ and $(22\bar{4}0)$ give the strongest reflexions in the prism zone, whilst among pyramidal forms $(13\bar{4}1)$ and $(12\bar{3}1)$ stand out by the intensity of their reflexions.

Oscillation photographs about c through 10° including the main prism face $(11\bar{2}0)$ showed lines at 8·1 Å., 4·05 Å., and 2·7 Å. Since $d_{11\bar{2}0}$ is thus $a/2$, a hexagonal lattice, as in the case of α-quinol, is indicated.

For the number of molecules per cell we have

$$n = \frac{5{\cdot}53 \times (16{\cdot}25)^2 \times \sqrt{3}/2 \times 1{\cdot}31}{110 \times 1{\cdot}65} = 9{\cdot}1,$$

i.e., 9 molecules. The maximum number of lattice-units required for the symmetry of a trigonal-polar crystal is three. Consequently each unit contains the substance of three molecules, three such units going to the cell. The three molecules in each unit have no symmetry, either in each molecule separately or in the three as a group. We have here, then, another such case of triple crystallographic association as in α-quinol (*loc. cit.*). In the present instance, three of the composite lattice-units are arranged about triad axes of symmetry throughout the crystal; but neither the lattice-units nor their orientations in the cell provide a plane of symmetry normal to the c axis. The space-group of β-quinol, finally, appears to be C_3^1.

γ-Modification of Quinol.—When quinol is crystallised by sublimation, a small proportion of the mainly acicular sublimate takes the form of thin leaflets having the contours of an acute-angled rhomb. Lehmann (*Z. Kryst. Min.*, 1877, 1, 43) found this polymorph, or γ-quinol, to be monoclinic-prismatic, with $\beta = 107°$, the flat face being (001) and the prism contours $\{11\bar{1}\}$. The present X-ray results entirely confirm this interpretation.

In density, 1·325, and m. p., 169°, the crystal resembles α-quinol rather than β-quinol. The leaflets frequently undergo spontaneous distortion within a few hours of being prepared, and gradually become opaque in the course of a few weeks; hence this modification of quinol does not appear to be stable at the ordinary temperature.

Rotation-photographs about the axes set up by Lehmann provided the following data:

Cell-dimension along a (mean of 6 spots on 4 layer-lines): $a = 13{\cdot}24$ Å.
" " b (" 5 " 2 "): $b = 5{\cdot}20$ Å.
" " c (" 6 " 3 "): $c = 8{\cdot}11$ Å.

The number of molecules per cell is given by

$$n = \frac{13{\cdot}24 \times 5{\cdot}20 \times 8{\cdot}11 \times \sin 73^\circ \times 1{\cdot}325}{110 \times 1{\cdot}65} = 3{\cdot}95,$$

i.e., 4 molecules. In the rotation photographs, the strongest reflexion was from (002), with weaker ones from (004) and (006), and none from odd orders of the base. Reflexions of more than average intensity were also given by (001), (012), and (200). No halvings of (*hkl*) planes could be traced, but (010) is halved, and (*hol*) planes in which either *h* or *l* is odd. It may be inferred, therefore, that the γ-quinol crystal falls into space-group C_{2h}^5, and is built up on the simple lattice Γm.

The proximate data for the crystal structure of quinol are thus at hand, and further methods of investigation will lead to an understanding of the arrangement of atoms and molecules in the several crystals. It is seen that although quinol, like most organic substances, can crystallise in unimolecular units and monoclinic symmetry (γ-quinol), yet it tends in its stabler forms (α- and β-quinol) to associate in termolecular units and to crystallise in the trigonal system. In its trigonal modifications, quinol, like the trigonal crystals quartz (Bragg and Gibbs, *Proc. Roy. Soc.*, 1925, *A*, **109**, 405) and carborundum (Ott, *Z. Krist.*, 1926, **63**, 1), shows a tendency to preserve certain simple axial relations in its passage from one polymorph to another. Thus the *c* axes of α- and β-quinol are almost the same, whilst the respective *a* axes are nearly in the ratio of 4 to 3. The better reflecting power of the planes in β-quinol than of those in α- and γ-quinol is another datum which, although its exact bearing is not clear at present, must play its part in the ultimate interpretation of these crystals.

The author desires to thank Sir William Bragg, F.R.S., for the interest he has taken in this work and for his valuable suggestions.

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[*Received, March 23rd,* 1927.]

CXLVIII.—*A Study of the Chemiluminescence of Phosphorus Vapour.*

By Edmund John Bowen and Edward George Pells.

The following work on the luminescence of phosphorus vapour in oxygen was an attempt to compare the number of molecules reacting chemically with the number emitting visible light during the process. The radiation emitted by glowing phosphorus vapour consists of a continuous band extending throughout the visible region (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235), a band spectrum in the near ultra-violet (Emeléus and Downey, J., 1924, **125**, 2491), and very probably wave-lengths less than 1800 Å. capable of ozonising oxygen. The distribution of energy in these different regions is not known.

The number of molecules producing light during the phosphorescence was determined by measuring photographically the number of quanta of light emitted. One part of a panchromatic plate was exposed to the glow and another part to the light from a tungsten filament lamp passed through a copper sulphate–ferrous sulphate filter to remove infra-red radiation. Equality of blackening on the plate was taken to indicate equality of luminous energy falling on the plate in the two cases. This assumption depends on the similarity of the distribution of energy in the visible region of the spectrum of glowing phosphorus vapour and of the filtered light from the tungsten lamp. It was shown to be justified to a sufficient degree of accuracy by photographs of the two sources of light through glass filters supplied by Messrs. Chance Bros. The following table gives the results :

Transmission region of glass filter (Å.) ……	7000—5300	6000—4800	4900—4000	3800—3200
Relative blackening for tungsten lamp ………	4	1	2	0
Relative blackening for phosphorus glow ……	4	2	1	0

Within a factor of less than 2, equal blackening therefore seemed to indicate equal quantities of energy incident on the plate from the two light sources.

The energy per second in the light from the tungsten lamp was measured with a thermopile calibrated in the usual way with a Hefner lamp. When the panchromatic plate was exposed to the light it was placed much farther away than the thermopile, and the incident energy was calculated by the inverse-square law. The same law was also used, although it is only approximate because of the large size of the light source, in calculating the total luminous energy radiated by the glowing phosphorus vapour from the blackening on the plate placed a known distance away.

In the first series of experiments the white phosphorus was contained in a thin layer, obtained by distillation in a high vacuum, on one half of the inside of a glass bulb about 2 cm. in diameter, which was immersed in water at a suitable temperature. The panchromatic plate was placed a short distance above the bulb. The bulb was connected to a larger bulb to act as a reservoir and to a McLeod gauge. Pure oxygen was admitted to the reservoir and gauge, the initial pressure measured, and the gas allowed to enter the phosphorus bulb. The glow filled the whole bulb, indicating that the reaction was between the oxygen and the phosphorus vapour (Rayleigh, *Proc. Roy. Soc.*, 1924, *A*, **106**, 1). When the reaction had proceeded for a definite time the residual pressure was measured. The glow seemed to remain fairly constant during each experiment, although in different experiments the rate of oxygen absorption varied greatly, apparently depending on the rate of volatilisation of the phosphorus as controlled by variation in a thin crust of oxide on the surface of the solid.

The following are the mean results obtained in three series of experiments:

1. Initial oxygen pressure = 5·17 mm.

Blackening on plate by phosphorus glow corresponds (from tungsten lamp–thermopile calibration) to $1{\cdot}76 \times 10^{-6}$ cal. per sq. cm.

Fraction of glow received on 1 sq. cm. of plate = $1/16\pi$ (approx.). Therefore total luminous energy emitted as phosphorescence = $8{\cdot}85 \times 10^{-5}$ cal.

If $h\nu = 8{\cdot}3 \times 10^{-20}$ cal. be taken as a mean energy of a quantum in the visible region, number of quanta emitted during the glow = $1{\cdot}06 \times 10^{15}$.

Number of molecules of oxygen absorbed

$$= 6 \times 10^{23} \times (\text{vol. of apparatus})(\text{cm. } O_2 \text{ absorbed})/76 \times 23{,}000$$
$$= 3{\cdot}42 \times 10^{19}.$$

The final product of oxidation is phosphoric oxide, produced as a result of a series of consecutive reactions; of these we may assume that only one emits light, and that it probably involves only one molecule of oxygen. If this is so, one-fifth of the oxygen molecules reacting may be taken as the number concerned in the luminescent stage.

If r represents the ratio of the number of such molecules to the number of quanta of light emitted, we have

$$r = 6{\cdot}8 \times 10^{18}/1{\cdot}06 \times 10^{15} = 6{\cdot}4 \times 10^{3}.$$

2. Initial oxygen pressure = $3{\cdot}5$ mm.
Number of quanta emitted during the glow = 4×10^{14}.
Total number of molecules of O_2 absorbed = $3{\cdot}4 \times 10^{19}$.

$$r = 6{\cdot}8 \times 10^{18}/4 \times 10^{14} = 1{\cdot}7 \times 10^{4}.$$

3. Initial oxygen pressure = $1{\cdot}18$ mm.
Number of quanta emitted during the glow = $1{\cdot}42 \times 10^{15}$.
Total number of molecules of O_2 absorbed = $2{\cdot}4 \times 10^{19}$.

$$r = 4{\cdot}8 \times 10^{18}/1{\cdot}42 \times 10^{15} = 3{\cdot}4 \times 10^{3}.$$

An important source of error in these experiments was the possible reaction of some of the oxygen with the solid phosphorus present, *i.e.*, the combination might not take place wholly in the vapour phase. To eliminate this, another series of experiments was performed. Phosphorus was vaporised at about 25° in a current of pure dry nitrogen and the gas passed into a small warmed bulb into which oxygen was allowed to leak. The glow in the vessel was photographed as before. To secure greater accuracy of comparison a neutral optical wedge was used in front of the plate for the exposure to the calibrated lamp, the times of exposure to the glow and to the lamp being the same. The amount of oxygen reacting with the phosphorus vapour was found by drawing the gases into a small vessel cooled in carbonic acid snow, and weighing the oxide deposited. The results of four experiments are given below :

Energy from lamp = $2{\cdot}5 \times 10^{-6}$ cal. per sec. per sq. cm. of plate.
Fraction of glow received on 1 sq. cm. of plate = $0{\cdot}05$.

Ratio of energy : glow/lamp.	Quanta emitted as luminescence per sec.	P_4O_{10} collected in 30 mins. (g.).	Molecules produced per sec.	Ratio Mols./Quanta.
1/10	6×10^{13}	0·121	$13{\cdot}1 \times 10^{16}$	$2{\cdot}18 \times 10^{3}$
1/8	$7{\cdot}5 \times 10^{13}$	0·126	$13{\cdot}6 \times 10^{16}$	$1{\cdot}81 \times 10^{3}$
1/10	6×10^{13}	0·129	$13{\cdot}9 \times 10^{16}$	$2{\cdot}32 \times 10^{3}$
1/12	$5{\cdot}2 \times 10^{13}$	0·121	$13{\cdot}1 \times 10^{16}$	$2{\cdot}52 \times 10^{3}$

These results are in agreement with those obtained by the previous method, and indicate that at least one in 2000 of the P_4 molecules undergoing oxidation emits a quantum of visible light. The agreement between the two series of experiments, however, must be viewed in the light of the assumptions made in the first series and of the possible effect of nitrogen on the glow in the second. As the light emitted is partly obscured by the cloud of solid oxide formed, the proportion of luminescent molecules is probably greater; also the number of molecules emitting ultra-violet light is not given by these experiments. Rayleigh (*loc. cit.*) has shown that the oxidation of phosphorus vapour with luminescence is a catalytic phenomenon occurring at the surface of solid oxide particles. The results of this paper on the fairly large proportion of luminescent molecules in the oxidation, when account is taken of the losses of light and of ultra-violet light emitted, seem to be most simply interpreted by assuming that the glow of phosphorus is a chemiluminescence of the type described by Kautsky (*Trans. Faraday Soc.*, 1926, **21**, 591). In his experiments, dyes adsorbed on a surface of siloxen undergoing oxidation were excited to emit their fluorescent spectrum as chemiluminescence. If the theory is extended to the case of phosphorus, it must be assumed that oxidation at the surface of solid particles of an oxide excites to luminescence adsorbed molecules of some other oxide. A large number of chemiluminescence phenomena are associated with reactions on solid particles, two well-defined cases being the oxidation of phosphorus and the oxidation of the dithiocarbonic acid esters. The curious phenomenon of the glow and explosion of so-called pure phosphine and oxygen mixtures when the pressure is suddenly reduced (van 't Hoff, " Studies in Chemical Dynamics," 1896), which has been shown by Emeléus (J., 1925, **127**, 1362) to emit the spectrum of glowing phosphorus, can only be reasonably explained by the catalytic effect of solid hydrogen phosphides or other particles deposited by the sudden cooling.

An interesting calculation is the " efficiency " of the oxidation of phosphorus as a light producer. The heat of formation of 1 g.-mol. of P_4O_{10} is 740,000 cals. A g.-mol. quantum of green light is 50,000 cals., whence, during phosphorescence,

$$\text{Energy of light/Total energy} = 3 \times 10^{-5}.$$

This is not a very high efficiency when compared with that for a candle, 10^{-2}; an electric lamp, 10^{-1}; or a mercury-vapour lamp, 0·5.

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[*Received, March 30th*, 1927.]

CXLIX.—*αβ-Dichloro-β-bromovinyl Ethyl Ether.*

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BY brominating αβ-dichlorovinyl ethyl ether and then heating the addition product, Crompton and Triffitt (J., 1921, **119**, 1874) obtained chlorobromoacetyl chloride. If the addition product is not heated but is treated at once with alcoholic potash, *αβ-dichloro-β-bromovinyl ethyl ether* is obtained in good yield :

$$\mathrm{CHCl{:}CCl{\cdot}OEt + Br_2 = CHClBr{\cdot}CClBr{\cdot}OEt.}$$

$$\mathrm{CHClBr{\cdot}CClBr{\cdot}OEt + KOH = CClBr{:}CCl{\cdot}OEt + KBr + H_2O.}$$

This ether resembles αβ-dichlorovinyl ethyl ether in its reactions towards ethyl alcohol and phenol (compare Crompton and Vanderstichele, J., 1920, **117**, 691). The reactions, however, take place less readily, considerable heating being necessary to induce the ether to react. The reactions with ethyl alcohol, phenol, β-naphthol, and quinol were studied and in each case gave rise to the corresponding ester :

$$\mathrm{CClBr{:}CCl{\cdot}OEt + R{\cdot}OH = CHClBr{\cdot}CO_2R + EtCl.}$$

The ether was also found to resemble αβ-dichlorovinyl ethyl ether in its reactions with acids, concentrated sulphuric acid, glacial acetic acid, and benzoic acid being selected as typical acids for the comparison. In each case ethyl chlorobromoacetate was obtained and, in the latter two cases, the acid chlorides of the reacting acids :

$$\mathrm{CClBr{:}CCl{\cdot}OEt + R{\cdot}CO_2H = CHClBr{\cdot}CO_2Et + R{\cdot}COCl.}$$

In the experiment with glacial acetic acid a secondary reaction took place on prolonged heating. No acid chloride could then be detected, but in addition to ethyl chlorobromoacetate considerable quantities of ethyl acetate and chlorobromoacetic acid were obtained.

When brominated, αβ-dichloro-β-bromovinyl ethyl ether gave *αβ-dichloro-αββ-tribromodiethyl ether*, which on exposure to moist air readily lost its halogen and passed into oxalic acid. On being heated in the absence of moisture, the ether was converted into chlorodibromoacetyl chloride, a reaction which also took place slowly on allowing the compound to remain in a sealed tube for several weeks at the ordinary temperature.

$$\mathrm{CClBr_2{\cdot}CClBr{\cdot}OEt \longrightarrow CClBr_2{\cdot}COCl + EtBr.}$$

Chlorine appeared to act on αβ-dichloro-β-bromovinyl ethyl ether in a similar manner.

EXPERIMENTAL.

αβ-Dichloro-β-bromovinyl Ethyl Ether.—To 100 g. of αβ-dichlorovinyl ethyl ether (Crompton and Vanderstichele, J., 1920, **117**, 691), cooled in a freezing mixture of ice and salt, 34 c.c. of bromine were run in slowly, the coloration then being permanent. The product was added to a solution of potassium hydroxide (60 g. of KOH, 40 c.c. of water, 310 c.c. of absolute alcohol) and, after ½ hour, sodium bromide having separated, the mixture was poured into 2 l. of water. The oil thus produced was washed with water, dried over soda-lime, and fractionally distilled, 100 g., b. p. 172—177°, being obtained. *αβ-Dichloro-β-bromovinyl ethyl ether* is a colourless liquid, b. p. 177°/754 mm., $d_{4^\circ}^{20^\circ}$ 1·6565, $d_{4^\circ}^{26^\circ}$ 1·6478, $d_{4^\circ}^{30^\circ}$ 1·6422, $n_{\mathrm{D}}^{17\cdot5^\circ}$ 1·50427; whence $[R_L]_{\mathrm{D}}^{17\cdot5^\circ}$ 39·24 (Found : Cl, 32·1; Br, 36·2. $C_4H_5OCl_2Br$ requires Cl, 32·2; Br, 36·3%).

Ethyl alcohol, phenol, and β-naphthol, by interaction with this ether, gave ethyl, phenyl, and β-naphthyl chlorobromoacetate, respectively, the product being identified in each case by its physical properties and by analysis. Quinol gave quinol bischlorobromoacetate, m. p. 122—123°. Concentrated sulphuric acid gave ethyl chlorobromoacetate, whereas acetic acid and benzoic acid yielded ethyl chlorobromoacetate together with acetyl chloride and benzoyl chloride, respectively, the acid chlorides being identified by conversion into the corresponding anilide and amide.

Action of Bromine on αβ-Dichloro-β-bromovinyl Ethyl Ether.—The ether (80 g.) was brominated at 0°, *αβ-dichloro-αββ-tribromodiethyl ether* separating as a solid. After recrystallisation from light petroleum, this ether (yield 82 g.) had m. p. 28—29°, $d_{4°}^{31°}$ 2·2297, $d_{4°}^{40°}$ 2·2138, $n_{\mathrm{D}}^{34°}$ 1·56833; whence $[R_L]_{\mathrm{D}}^{34°}$ 55·88 (Found: Cl, 18·8; Br, 63·9. $C_4H_5OCl_2Br_3$ requires Cl, 18·7; Br, 63·2%). It is readily soluble in the cold in acetone, alcohol, carbon tetrachloride, benzene or xylene, and insoluble in cold or hot water.

Action of Heat on αβ-Dichloro-αββ-tribromodiethyl Ether.—The ether was heated at about 60° in a hard glass tube drawn out to a fine capillary. Ethyl bromide was evolved and the ether changed almost quantitatively into chlorodibromoacetyl chloride. This was identified by conversion into chlorodibromoacetamide, which, mixed with an authentic specimen, melted at 127—128°. The acid chloride was further characterised by conversion into the *anilide*, which, after crystallisation from aqueous alcohol, melted at 102—103° (Found: N, 4·4. $C_8H_6ONClBr_2$ requires N, 4·3%).

Action of Chlorine on αβ-Dichloro-β-bromovinyl Ethyl Ether.—Dry chlorine was readily absorbed by αβ-dichloro-β-bromovinyl ethyl ether at 0°, but the product could not be obtained crystalline, nor any uniform material by distillation under reduced pressure. On exposure to moist air, the product was largely converted into oxalic acid; and when it was heated at 60° for several hours in a tube drawn out to a capillary, dichlorobromoacetyl chloride (identified by conversion into dichlorobromoacetamide) was formed. These results indicated the presence of ααββ-tetrachloro-β-bromodiethyl ether, but this could not be isolated.

Molecular Refractivities.—The molecular refractivity of αβ-dichloro-β-bromovinyl ethyl ether, obtained from the observed refractivity by the Lorenz and Lorentz formula, is slightly lower than that calculated by means of Eisenlohr's atomic refractivities, and that of αβ-dichloro-αββ-tribromodiethyl ether is somewhat higher. The refractivities of the allied compounds αβ-dichlorovinyl ethyl ether and αββ-trichlorovinyl ethyl ether were therefore determined for comparison; the former has $d_{4°}^{20°}$ 1·2037, $d_{4°}^{25°}$ 1·1972, $d_{4°}^{30°}$ 1·1909,

$n_D^{16\cdot5^\circ}$ 1·45584, and the latter has $d_{4^\circ}^{20^\circ}$ 1·3409, $d_{4^\circ}^{25^\circ}$ 1·3343, $d_{4^\circ}^{30^\circ}$ 1·3280, $n_D^{16^\circ}$ 1·47551.

	$[R_L]_D$.		
	Found.	Calc.	Diff.
αβ-Dichloro-β-bromovinyl ethyl ether	39·24	39·35	−0·11
αβ-Dichlorovinyl ethyl ether	31·71	31·582	+0·13
αββ-Trichlorovinyl ethyl ether	36·73	36·449	+0·28
αβ-Dichloro-αββ-tribromodiethyl ether	55·88	55·34	+0·54

The somewhat anomalous behaviour of αβ-dichloro-β-bromovinyl ethyl ether may be connected with the *cis-trans* isomerism which it should exhibit, but attempts to isolate the isomerides from the product prepared as above were not successful.

The author desires to express her thanks to Mr. Holland Crompton for much advice and criticism.

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[*Received, March 2nd*, 1927.]

CL.—*The Basic Character of the Acetoxylidides and its Influence on the Course of their Substitution.*

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IN continuance of earlier work on substituted diphenic acids, it was desired to examine diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid (Mayer, *Ber.*, 1911, **44**, 2301) and its derivatives. During the preparation of the *m*-2-xylidine required for this purpose, an interesting property of its acetyl derivative was observed. In one experiment, for example, in which aceto-*m*-2-xylidide had been boiled with 6 litres of concentrated hydrochloric acid, 440 g. crystallised when the solution was diluted with an equal bulk of water and cooled, but a further 200 g. were precipitated when the liquor was neutralised. Although such treatment with hydrochloric acid is a very usual method of purifying the compound, its very noteworthy basicity seems completely to have escaped notice by previous workers and is not mentioned in the recent paper of Morgan and Hickinbottom (*J. Soc. Chem. Ind.*, 1926, **45**, 2228). It is in fact sufficiently pronounced to permit of the preparation of salts by mixing the acetyl derivative with moderately concentrated mineral acids. The *hydrobromide* and *nitrate*, thus obtained, are stable substances, but the hydrochloride gradually loses hydrogen chloride on exposure to the air. Characteristically crystalline, stable hydrobromides of aceto-*m*-4-, -*p*-, -*o*-3-, and -*o*-4-xylidides and of acetomesidide have been similarly prepared and analysed, so that it would appear that the basic properties of these acetyl derivatives are due at least in part to the general effect of the introduction of methyl groups into the molecule, irrespective of their orientation. Although salts of acetanilide have been prepared, they are unstable in presence of water (Noelting and Weingärtner, *Ber.*, 1885, **18**, 1340; Wheeler, Barnes, and Pratt, *Amer. Chem. J.*, 1897, **19**, 676; Knorr, *Annalen*, 1888, **245**, 375).

Whilst it will be of interest to pursue this matter further in a general manner, it has been first followed up more particularly in connexion with the original purpose of these experiments, namely, the formation of substitution derivatives of *m*-2-xylidine. Previous workers had shown that bromination of the base in glacial acetic acid solution occurs, as might be expected, in the 5-position, but that 4-nitro-derivatives are obtained from both the base and its acetyl derivative (Noelting and Stoecklin, *Ber.*, 1891, **24**, 568; Noelting, Braun, and Thesmar, *Ber.*, 1901, **44**, 2259). Our observations on salt formation suggested that this might be the factor determining the course of nitration, and the idea gained credence when it was found that bromination of the acetyl derivative in chloroform solution occurs in the 5-position, in glacial acetic acid solution chiefly in the 5- but also, as Noelting and Pick had observed, in the 4-position, and in hydrobromic or sulphuric acid suspension very largely, if not solely, in the 4-position. We therefore expected to be able to obtain 5-nitro-*m*-2-xylidine by the use of m-*nitrobenzo*-m-2-*xylidide*. Although, however, this compound is not noticeably basic in character, it also yielded a 4-*nitro*-derivative, whether sulphuric acid were present or not. This result perhaps does not entirely exclude salt formation as a contributory factor in the behaviour of the acetyl derivative, but it is clearly not a necessary one. This became still more apparent when it was found that bromination of the free base in presence of hydrobromic acid, as of acetic acid, occurs in the 5-position.

The complexity of the problem was not diminished when, for purposes of comparison, the behaviour of *m*-4-xylidine was considered. Although the directive influences in this compound and its derivatives would be expected to accord very closely with those in their 2-isomerides, the two series are not in all respects analogous in behaviour. Whilst, for example, bromination of the base in glacial acetic acid solution occurs in the 5-position (Noelting, Braun, and Thesmar, *loc. cit.*), its acetyl derivative is attacked in the 6-position (Genz, *Ber.*, 1870, **3**, 225; Noelting, Braun, and Thesmar, *loc. cit.*). Not only have we confirmed the latter observation, but we have also found that the result is the same in chloroform solution, as well as in presence of hydrobromic acid. Again, not only the base, but also its acetyl derivative, in presence of sulphuric acid suffers nitration in the 6-position, whereas nitric acid alone converts the acetyl derivative into 5-nitroaceto-*m*-4-xylidide. By similar variations of experimental conditions, 5- or 6-*nitro*-derivatives are obtained from m-*nitrobenzo*-m-4-*xylidide*, but, as already mentioned, this is not applicable to the 2-isomeride.

There would seem to be no very obvious way of embracing these results within one generalisation, so that detailed discussion may be reserved until the behaviour of the other xylidines has been examined. But it would seem that even in the commonest forms of substitution, as well as in mercuration (Coffey, J., 1925, **127**, 1029; Burton, Hammond, and Kenner, J., 1926, 1802), the nature of the entering substituent requires consideration. Also it is clear that the widely accepted doctrine of salt formation as a determining factor on the course of the nitration of amines is at least not unreservedly applicable to every case.

EXPERIMENTAL.

On the addition of hydrobromic acid, b. p. 126°, to aceto-*m*-2-xylidide, the compound passed into solution, but almost immediately small needles of the *hydrobromide* separated (Found: N, 6·0; equiv., 245. $C_{10}H_{13}ON,HBr$ requires N, 5·7%; equiv., 244). By dilution with water a clear solution was obtained, from which the original acetyl derivative was precipitated on the addition of alkali. (This observation applies equally to the other salts to be described.) In each case the salt was prepared for analysis by thoroughly draining it on porous earthenware and finally drying it in a vacuum over solid potassium hydroxide for 12 hours. The *nitrate* was obtained in hexagonal prisms by use of a mixture of nitric acid (*d* 1·42) with three volumes of water (Found: N, 12·4; equiv., 226·3. $C_{10}H_{13}ON,HNO_3$ requires N, 12·4%; equiv., 226). The sulphate also was prepared, but it could not be completely freed from sulphuric acid. *Aceto*-m-4-*xylidide hydrobromide* formed minute prisms (Found: equiv., 247). *Aceto*-m-4-*xylidide hydrochloride* separated from concentrated hydrochloric acid in plates (Found: equiv., 202. $C_{10}H_{13}ON,HCl$ requires equiv., 199·5). *Aceto*-p-*xylidide hydrobromide* forms hexagonal leaflets (Found: equiv., 243), and *aceto*-o-3-*xylidide hydrobromide* rectangular plates (Found: equiv., 247). *Aceto*-o-4-*xylidide hydrobromide*, prismatic crystals, is hydrated (Found: equiv., 261). Acetomesidide was prepared by Feith and Davies (*Ber.*, 1891, **24**, 3546) from the oxime of methyl mesityl ketone, but it can also be easily obtained by boiling a solution of the base (4 g.) in benzene (10 c.c.) with acetic anhydride (4 c.c.). It also furnished a stable *hydrobromide*, which crystallised in small, hexagonal prisms (Found: equiv., 256. $C_{11}H_{15}ON,HBr$ requires equiv., 258).

Substitution in m-2-*Xylidine and its Derivatives.*

Bromination Experiments.—For the purpose of these experiments, authentic 4-bromo-*m*-2-xylidine was prepared by Noelting, Braun, and Thesmar's method (*Ber.*, 1901, **34**, 2261). In this connexion, 4-nitro-*m*-2-xylidine was conveniently converted into 2 : 4-dinitro-*m*-xylene by oxidising a suspension of the base (10 g.) in ice-water (375 g.) with the paste prepared from potassium persulphate (50 g.) and sulphuric acid (100 g.), and oxidising the resulting crude nitroso-derivative with nitric acid (*d* 1·48; 75 c.c.) at 40—45°. Reduction of the dinitro-compound by ammonium sulphide as prescribed by the above authors is very slow and is much more effectively achieved by gradual addition of a solution prepared from crystallised (the commercial product gives less satisfactory results) sodium sulphide (7·5 g.), sulphur (2 g.), and water (30 c.c.) to a boiling suspension of the dinitro-compound (5·8 g.) in water (200 c.c.). Furthermore, the use of tin and hydrochloric acid (17 c.c.) was found more satisfactory for reduction of 4-bromo-3-nitro-*m*-xylene (8 g.) than the procedure adopted by Noelting, Braun, and Thesmar.

(*a*) When a solution of aceto-*m*-2-xylidide (2 g.) and bromine (2 g.) in chloroform (10 c.c.) was left in contact with iron wire at the ordinary temperature for 12 hours, the product was 5-bromoaceto-*m*-2-xylidide (Found: N, 5·85%), which was obtained in the pure condition (m. p. 194—195°) after one crystallisation from alcohol.

(*b*) On the other hand, if the acetyl derivative and bromine in the same proportion were allowed to interact at the ordinary temperature for ½ hour in glacial acetic acid (20 c.c.), the 5-bromo-derivative was obtained in the pure condition only after two crystallisations from dilute alcohol, and fractions of lower melting point were recovered from the mother-liquors. These were not further investigated in view of the definite statement of Noelting, Braun, and Thesmar (*loc. cit.*, p. 2262) that the 4-bromo-derivative is also produced under such conditions.

(*c*) The finely ground suspension resulting from the mixture of aceto-*m*-2-xylidide (12 g.) with hydrobromic acid (b. p. 126°; 120 c.c.) was first converted at the ordinary temperature by addition of bromine (12 g.) into a pasty mass, which resolidified after some time. The product collected after 12 hours was 4-bromoaceto-*m*-2-xylidide (12 g.), which was obtained in the pure condition after two crystallisations from dilute alcohol. It then melted at 135—136° and did not depress the melting point of an authentic specimen. A similar result was obtained when sulphuric acid (110 c.c.) was employed in place of the hydrobromic acid. Since the melting-point test of identity is sometimes fallible, the nature of the product was further established by hydrolysing it (10 g.) by boiling for 4 hours with 50% sulphuric acid (although Noelting, Braun, and Thesmar, *loc. cit.*, p. 2260, state that they were unable to effect a satisfactory hydrolysis). The base (6·5 g.), b. p. 159—161°/24—25 mm., furnished a m-*nitrobenzoyl* derivative, which separated from alcohol in small rosettes, m. p. 170—171° (Found : N, 8·15. $C_{15}H_{13}O_3N_2Br$ requires N, 8·0%). Its melting point was depressed by addition of the isomeric compound described below.

(*d*) Bromination of *m*-2-xylidine in presence of glacial acetic acid was found by Noelting, Braun, and Thesmar to furnish the 5-bromo-derivative, but no yield was recorded. Repetition of their experiment gave the pure material in a yield of 88%, and no indication of the 4-isomeride was obtained on acetylation.

(*e*) Again, the addition of bromine (8 g.) to a solution of the base (6 g.) in hydrobromic acid (b. p. 126°; 40 c.c.) at 15—20° yielded the 5-bromo-derivative, together with some oily material (2·3 g.). This oil was recovered by extraction of the porous earthenware used to dry the crude product, and on acetylation it was found to consist essentially of the 5-bromo-base. This was further characterised by its m-*nitrobenzoyl* derivative, which separated from dilute acetic acid in long needles, m. p. 186—187° (Found : N, 8·2. $C_{15}H_{13}O_3N_2Br$ requires N, 8·0%).

Chlorination Experiments.—4-*Chloro*-2-*nitro*-m-*xylene*, prepared from 2-nitro-*m*-4-xylidine, separated from alcohol in yellow needles, m. p. 72—73° (Found : N, 7·9. $C_8H_8O_2NCl$ requires N, 7·5%). It was converted by means of tin and hydrochloric acid into 4-*chloro*-m-2-*xylidine*, b. p. 136—138°/17 mm. (Found : N, 9·1. $C_8H_{10}NCl$ requires N, 9·0%). 4-*Chloroaceto*-m-2-*xylidide* crystallises from dilute alcohol in white needles, m. p. 146—147° (Found : N, 7·2. $C_{10}H_{12}ONCl$ requires N, 7·1%).

5-*Chloro*-2-*nitro*-m-*xylene*, prepared from 2-nitro-*m*-5-xylidine, forms plates, m. p. 44—45° (Found : N, 7·75%). 5-*Chloro*-m-2-*xylidine* crystallises in long, silky needles, m. p. 44—45° (Found : N, 9·0%); it was characterised by its *acetyl* derivative, which separates from dilute alcohol in plates, m. p. 195° (Found : N, 7·0%).

A solution of *m*-2-xylidine (25 g.) in glacial acetic acid (150 c.c.) was treated at 10—15° with dry chlorine, generated from potassium permanganate (15 g.). After 2 hours, the dark blue mixture was diluted, rendered alkaline, and distilled in steam. The first portion of distillate was separated as likely to contain any unchlorinated material, and the oil in it did not solidify. Subsequent portions, however, solidified and furnished 5-chloro-*m*-2-xylidine (15 g.),

m. p. 42°, which was identified by direct comparison with authentic base. A considerable proportion of the material was not volatile in steam, and probably consisted of more highly chlorinated material. Similar results are well known to follow chlorination of the toluidines and their acetyl derivatives, and render chlorinations not very suitable for the present purpose. For the time, therefore, this method was not further pursued.

Nitration Experiments.—(*a*) m-*Nitrobenzo*-m-2-*xylidide*, prepared from *m*-2-xylidine and *m*-nitrobenzoyl chloride in presence of pyridine, separated from alcohol in needles, m. p. 188—189° (Found: N, 10·6. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). A mixture of nitric (*d* 1·42; 1·6 g.) and sulphuric (10 g.) acids was added at 0° to a solution of *m*-nitrobenzo-*m*-2-xylidide (6·5 g.) in sulphuric acid (20 g.). The product was isolated after 12 hours in small, yellow needles, m. p. 165—166° (5·5 g.) after crystallisation from alcohol. Its constitution was established both by its identity with authentic m-*nitrobenzo*-4-*nitro*-m-2-*xylidide*, m. p. 170·5°, prepared from 4-nitro-*m*-2-xylidine (Found: N, 13·5. $C_{15}H_{13}O_5N_3$ requires N, 13·3%), and by hydrolysis with 75% sulphuric acid to 4-nitro-*m*-2-xylidine, m. p. 81°.

(*b*) A similar result was obtained when the m-*nitrobenzoyl* derivative (3 g.) was dusted into nitric acid (*d* 1·42; 15 c.c.) at 25°, and the temperature finally allowed to rise to 50°.

Substitution in m-4-*Xylidine and its Derivatives.*

Bromination Experiments.—(*a*) The statement that aceto-*m*-4-xylidide undergoes bromination in the 6-position in glacial acetic acid solution (Genz, *loc. cit.*; Noelting, Braun, and Thesmar, *loc. cit.*) was confirmed.

(*b*) A mixture of bromine (4 g.) with aceto-*m*-4-xylidide (4 g.) and hydrobromic acid (b. p. 126°; 60 c.c.) was not decolorised even after 8 days. The product, after repeated crystallisation from dilute alcohol, yielded 6-bromoaceto-*m*-4-xylidide (1 g.), m. p. 168—169°, whilst by hydrolysis of the residues with 50% sulphuric acid 1 g. of the corresponding base, m. p. 96—97°, was recovered.

(*c*) The acetyl derivative (5 g.) was very slowly attacked at the ordinary temperature by bromine (5 g.) in chloroform solution (50 c.c.) in presence of iron wire. The product, isolated after 24 hours, yielded 1 g. of 6-bromo-*m*-4-xylidine, m. p. 96—97°. Another experiment showed that bromination was far from complete even after 6 weeks.

Nitration Experiments.—(*a*) m-*Nitrobenzo*-m-4-*xylidide* forms white needles, m. p. 162—163° (Found: N, 10·4. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). The compound (3 g.) was dusted into nitric acid (*d* 1·42; 15 c.c.) at 5—10°, and the temperature was allowed to rise to 30°; the product, after crystallisation from glacial acetic acid, furnished 2·4 g. of material, m. p. 209—210°, identical with authentic m-*nitrobenzo*-5-*nitro*-m-4-*xylidide*, m. p. 210—211° (Found: N, 13·4. $C_{15}H_{13}O_5N_3$ requires N, 13·3%).

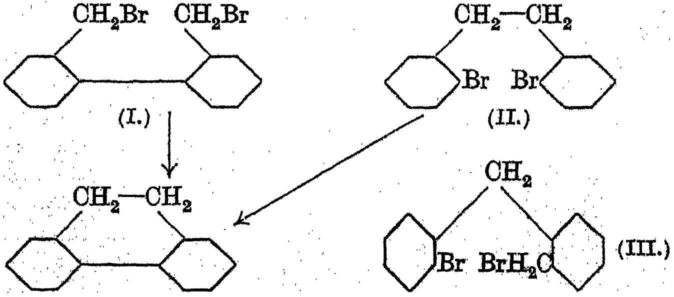
(*b*) Addition of a mixture of nitric acid (*d* 1·48; 1·6 g.) with sulphuric acid (10 g.) to a solution of *m*-nitrobenzo-*m*-4-xylidide (5 g.) in sulphuric acid (20 g.) at 0° furnished a product (5 g.), from which needles, m. p. 217—218°, were obtained by crystallisation from glacial acetic acid. The essential nature of the material followed from its identity with authentic m-*nitrobenzo*-6-*nitro*-m-4-*xylidide*, m. p. 224—225° (Found: N, 13·3%), and from its hydrolysis by alcoholic sodium hydroxide to 6-nitro-*m*-4-xylidine, m. p. 117—118°.

THE UNIVERSITY, SYDNEY. [*Received, March 9th*, 1927.]

CLI.—*Jackson and White's Synthesis of Phenanthrene.*

By JAMES KENNER and JOHN WILSON.

IT was shown some years ago (Kenner and Turner, J., 1911, **109**, 2101) that ωω′-dibromo-2 : 2′-ditolyl (I) is converted by treatment with sodium into a product from which, by oxidation, phenanthraquinone is obtained to the extent of 26% of that theoretically possible. At the same time it was pointed out that the initial material represents one of the possible intermediate products in the conversion of *o*-bromobenzyl bromide into a phenanthrene derivative through the agency of sodium.



The yield of phenanthraquinone obtained by Jackson and White (*Amer. Chem. J.*, 1880, 2, 383) in this manner amounted, however, to only 2·66%. On the other hand, consideration of the relative reactivities of the two bromine atoms in *o*-bromobenzyl bromide suggests 2 : 2′-dibromodibenzyl (II) as the compound most likely to be produced in the first stages of the reaction. Since, then, anthracene was isolated to the extent of nearly 20% of that theoretically possible, and presumably was derived from 2-bromophenyl-ω-bromo-*o*-tolylmethane (III), it appeared that the action of sodium on 2 : 2′-dibromodibenzyl must furnish as chief product some other compound than dihydrophenanthrene, and it became of interest to investigate this point experimentally.

The dibromo-compound was prepared by the reaction discovered by Busch and Weiss (*Ber.*, 1900, **33**, 2701), consisting in the oxidation of *as*-dibenzylhydrazines by mercuric oxide :

$$(CH_2Ph)_2N{\cdot}NH_2 + HgO = CH_2Ph{\cdot}CH_2Ph + N_2 + H_2O + Hg.$$

It was then found that 2 : 2′-*dibromodibenzyl* is converted by treatment with sodium to the extent of more than 50% into dibenzyl, accompanied by other products, including phenanthrene or its dihydro-derivative. By oxidation of the mixture, phenanthraquinone was obtained in a yield of 12% of that theoretically possible, calculated on the weight of the original material. Whilst, therefore, the earlier synthesis connected phenanthrene with ditolyl, the present work, like Pschorr's valuable general synthesis, shows its relationship to dibenzyl.

The formation of dibenzyl, which was also noted by Jackson and White in their experiments, represents a not uncommon type of side reaction in syntheses of this kind (compare Schlubach and Goes, *Ber.*, 1922, **55**, 2889) and is perhaps not surprising in this instance, since Ullmann (*Annalen*, 1904, **332**, 40) found that only a 5% yield of diphenyl is obtained from bromobenzene by the Fittig reaction. In dibromoditolyl, this stage of the synthesis is already achieved, so that a better yield of phenanthrene derivative is obtained from this compound.

By applying the above result to the data supplied by Jackson and White, it is possible to account for almost the whole of their material on the hypothesis that dibromodibenzyl is the source of the phenanthrene derivative obtained by them. Thus their yield of 2·66% involves conversion of 22·2% of the original material into dibromodibenzyl. Their observation that only 75·4% of the total available bromine was eliminated as sodium bromide would correspond to 49·2% of material of which debromination was only half complete. These amounts, together with 19·8% converted into anthracene and 12·5% into products of indeterminate character, account satisfactorily for all the material, and it may therefore be concluded that the phenanthrene derivative obtained by Jackson and White originated for the most part from dibromodibenzyl.

When the reaction between *o*-bromobenzyl bromide and hydrazine hydrate in alcoholic solution was carried out either at the ordinary temperature or at 100°, the desired product was accompanied by a considerable proportion of *tri*-o-*bromobenzylhydrazine*,

$$(C_6H_4Br\cdot CH_2)_2N\cdot NH\cdot CH_2\cdot C_6H_4Br \text{ (IV)},$$

and of non-basic material, corresponding in composition to o-*bromobenzylidenedi*-o-*bromobenzylhydrazone*,

$$(C_6H_4Br\cdot CH_2)_2N\cdot N\colon CH\cdot C_6H_4Br \text{ (V)}.$$

In their analogous preparation of dibenzylhydrazine, Busch and Weiss (*loc. cit.*) had similarly noted the formation of benzylidenebenzylhydrazone, and tentatively explained it by the equation :

$$2(CH_2Ph)_2N\cdot NH_2 = (CH_2Ph)_2N\cdot N\colon CHPh + CH_2Ph\cdot NH\cdot NH_2.$$

Although, in support of this view, they described the isolation of the hydrazone as a product of the reduction of dibenzylnitrosoamine, Busch and Weiss were unable to detect the benzylhydrazine formulated as the second product, and it will also be seen that the two sides of the equation do not balance. In our experiment, it seemed simpler to attribute the formation of (V) to oxidation of (IV), and in fact this reaction was shown to occur rapidly and quantitatively when the hydrochloride of (IV) was boiled in alcoholic solution with a little cupric oxide. Busch and Weiss observed the formation of tribenzylhydrazine in their experiment, whilst Franzen and Kraft (*J. pr. Chem.*, 1911, **84**, 157) showed that it could be obtained by direct benzylation of hydrazine, and also prepared it from benzylidenedibenzylhydrazone by reduction.

A further study of the reaction between benzyl chloride and hydrazine showed that some tribenzylhydrazine is produced even when the amount of hydrazine used is twice that required for dibenzylation, whilst when the reactants in equimolecular proportion were heated in alcoholic solution, the tribenzylhydrazine, which constituted the main product, was accompanied by some tetrabenzylhydrazine. This compound had previously been prepared by Wieland and Schomberg by treating tribenzylhydrazine with benzyl bromide (*Ber.*, 1920, **53**, 1329).

Finally, it was shown that tribenzylhydrazine hydrochloride could be oxidised to benzylidenedibenzylhydrazone by atmospheric oxygen in hot dilute alcoholic solution.

EXPERIMENTAL.

Comparative experiments showed decomposition of a solution of *o*-toluenediazonium bromide with Naturkupfer C, first at 0° and ultimately at 40°, to be the best method of preparing *o*-bromotoluene. Its monobromination was achieved very satisfactorily at 135° by adding 75% of the calculated quantity of bromine. *o*-Bromobenzyl bromide, separated by fractionation, boiled at 129°/19 mm.

Interaction of o-*Bromobenzyl Bromide and Hydrazine.*—When a cooled solution of the bromide (10 g.) in alcohol (15 c.c.) was treated with hydrazine hydrate (2·5 g.), a vigorous reaction occurred with evolution of heat and separation of an oily layer of aqueous hydrazine hydrochloride. This salt separated in needles after the mixture had been boiled for 1 hour and concentrated to one-third of the original bulk and the residue cooled. The other products were isolated by extracting the supernatant liquor with ether, after dilution with water (1 l.). When the dried ethereal solution was treated with an alcoholic solution of hydrogen chloride, *di*-o-*bromobenzylhydrazine hydrochloride* (3·5 g.), m. p. 205°, was precipitated. After purification by solution in alcohol (35 c.c.) and precipitation by ether (70 c.c.), it was obtained in matted, colourless needles, m. p. 214° (Found : N, 7·1; equiv., 406. $C_{14}H_{14}N_2Br_2,HC2$ requires N, 6·9%; equiv., 406·5). Its *benzylidene* derivative forms white plates, m. p. 116° (Found : N, 6·2. $C_{21}H_{18}N_2Br_2$ requires N, 6·1%).

Tri-o-*bromobenzylhydrazine hydrochloride*, which crystallises in hexagonal prisms, m. p. 194° (Found : N, 4·9. $C_{24}H_{19}N_2Br_3,HCl$ requires N, 4·9%), is soluble in a mixture of alcohol and ether. It separated from the mother-liquor after precipitation of dibromobenzylhydrazine hydrochloride in the manner just described. Both were, however, precipitated when dry hydrogen chloride was passed directly into the above dried ethereal solution. The tribromobenzyl derivative was rapidly oxidised in boiling alcoholic solution by cupric oxide, and gradually by atmospheric oxygen during recrystallisation, to o-*bromobenzylidenedi*-o-*bromobenzylhydrazine*, which formed prisms, m. p. 108° (Found : N, 5·4; Br, 44·9. $C_{21}H_{17}N_2Br_3$ requires N, 5·2; Br, 44·7%).

Synthesis of Phenanthraquinone.—2 : 2'-*Dibromodibenzyl* was obtained in almost quantitative yield by adding yellow mercuric oxide to a solution of dibromodibenzylhydrazine, prepared by shaking the hydrochloride with dilute sodium hydroxide solution and chloroform. It separated from alcohol in plates, m. p. 84·5° (Found : Br, 47·15. $C_{14}H_{12}Br_2$ requires Br, 47·1%).

When the dibromo-derivative (5 g.) was boiled under reflux with a suspension of sodium powder (5 g.) in dry ether for 14 days, 96·6% of the bromine was obtained in the ionic condition. On evaporation, the ethereal solution furnished an oil (2·60 g.), from which dibenzyl (1·42 g.) crystallised. This was purified by steam distillation and identified by comparison with an authentic specimen. In two concordant experiments, oxidation of the oil by a solution of chromic acid in glacial acetic acid, followed by the usual procedure for purification, yielded phenanthraquinone corresponding to 12% of that theoretically possible.

Interaction of Benzyl Chloride with Hydrazine.—(a) The observation that dibromodibenzylhydrazine yields a monohydrochloride rendered it necessary to examine the product described by Busch and Weiss as the dihydrochloride of dibenzylhydrazine. Analysis showed the salt, m. p. 202° (Busch and Weiss give m. p. 200°), to be a *monohydrochloride* (Found: N, 11·5; equiv., 249·5. $C_{14}H_{16}N_2$,HCl requires N, 11·3%; equiv., 248·5).

(b) In order to study its tendency to oxidise, tribenzylhydrazine was prepared by boiling benzyl chloride (22 g.), hydrazine hydrate (8·7 g.), and alcohol (25 c.c.) together for 1 hour and finally concentrating the mixture to one-third of its original bulk. Hydrazine hydrochloride separated on cooling; the filtrate was then diluted and extracted with ether. From the dried ethereal solution tribenzylhydrazine hydrochloride (22 g.), m. p. 181° (Found: N, 4·9%; equiv., 336), was obtained by treatment with alcoholic hydrogen chloride. Tetrabenzylhydrazine, m. p. 139° (Found: N, 7·3%), was isolated in small amount from the liquor.

When air was passed through a boiling solution of tribenzylhydrazine hydrochloride (1 g.) in alcohol (100 c.c.) for 8 hours, 0·25 g. of pure benzylidenedibenzylhydrazine, m. p. 87°, was obtained, whereas a quantitative yield was obtained after a few minutes in presence of cupric oxide. Dibenzylhydrazine hydrochloride, on the other hand, did not undergo atmospheric oxidation.

A series of experiments in which benzyl chloride was similarly treated with variously excessive proportions of hydrazine hydrate showed that the formation of tribenzylhydrazine and the corresponding hydrazone to a greater or less extent always accompanies that of dibenzylhydrazine. The formation of the hydrazone observed by Busch and Weiss may therefore safely be ascribed to oxidation of tribenzylhydrazine. Separation of the two hydrazine hydrochlorides was effected by taking advantage of the smaller solubility of the dibenzyl derivative in ether and by crystallising the tribenzyl derivative from alcohol.

This work was carried out during the tenure by one of us (J. W.) of a Town Trustee Fellowship at the University of Sheffield.

THE UNIVERSITY, SHEFFIELD. [*Received, March 9th,* 1927.]

CLII.—*Piperidine as a General Reagent for the Determination of the Constitution of Halogenonitro-compounds. The Nitration of 4 : 4′-Dihalogenodiphenylmethane and -s-diphenylethane.*

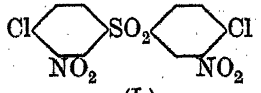
By Raymond James Wood Le Fèvre and Eustace Ebenezer Turner.

In this paper are described a number of piperidino-compounds the preparations and properties of which have led us to the conclusion that, as a reagent for reactive halogen atoms, piperidine is superior to alcoholic ammonia, aromatic amines, alkali alkyloxides, etc. The advantages contributing to this superiority include the following: (1) The substituted phenylpiperidines produced are as a rule highly crystalline. (2) Piperidine appears to react much more readily than most bases with mobile halogen atoms. (3) The interaction of piperidine and halogeno-compounds is generally characterised by the absence of by-products, whereas with hydrazines and alkali alkyloxides, for example, a mixture of products is usually obtained (compare Brand, *J. pr. Chem.*, 1903, **67**, 145; Lobry de Bruyn, *Rec. trav. chim.*, 1890, **9**, 203).

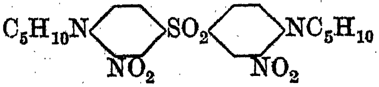
A few isolated piperidine compounds have been described in the past, notably by Lellmann and by Borsche. Lellmann was, however, not concerned with piperidine as a reagent, and Borsche, in employing piperidine, uses a method which in our hands has given most unsatisfactory yields (see Experimental).

Some examples follow illustrating the use of piperidine as a general reagent for reactive halogen atoms present in a number of compounds of known constitution.

The constitution (I) of the product of nitrating 4 : 4′-dichlorodiphenylsulphone was established by Ullmann and Korselt (*Ber.*, 1907, **40**, 643), using aniline and ammonia as reagents for reactive chlorine. Piperidine readily converts (I) into 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylsulphone* (II).



(I.)



(II.)

Similarly, 2 : 5-dibromonitrobenzene is converted by piperidine into 4-*bromo*-2-*nitropiperidinobenzene*. In the case of 2 : 4-dichloronitrobenzene both halogens rapidly react with piperidine to give 1-*nitro*-2 : 4-*dipiperidinobenzene*.

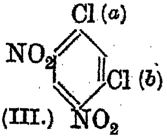
3 : 4-Dichloronitrobenzene would be expected to react once only

with piperidine and does so to give 2-*chloro*-4-*nitropiperidinobenzene*. 2 : 4 : 5-Trichloronitrobenzene, however, gives 4 : 5-*dichloro*-1-*nitro*-2-*piperidinobenzene* and not 5-chloro-1-nitro-2 : 4-dipiperidinobenzene, a fact which may be attributed to the combined steric and deactivating effects of the 5- on the 4-chlorine atom. The constitution of the product is proved below.

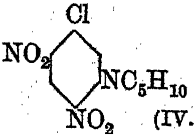
On the other hand, the introduction of a third group, *e.g.*, carboxyl or carbethoxyl, which by itself has feeble activating effect, produces a very marked exaltation of reactivity when its effect supports that of the nitro-group. Thus, towards piperidine, ethyl 2-chloro-5-nitrobenzoate, 4-chloro-3-nitrobenzoic acid, and 2 : 4-dichloronitrobenzene react apparently with the same vigour as does 1-chloro-2 : 4-dinitrobenzene.

The binuclear halogenonitro-compounds mentioned in this paper are all further examples of the same fact, *i.e.*, they react much more rapidly and completely than does either *o*- or *p*-chloronitrobenzene. Similarly, Borsche and Exss (*Ber.*, 1923, **46**, 2353) obtained quantitative results showing that 4-chloro-3-nitroazobenzene was intermediate between 1-chloro-2-nitro- and 1-chloro-2 : 4-dinitro-benzene in degree of reactivity.

The investigation of 1 : 3-dichloro-4 : 6-dinitrobenzene by previous workers has already raised many interesting points. Thus, Borsche and Bahr (*Annalen*, 1913, **402**, 81) considered that in this compound (III) one chlorine atom (*a*) is less reactive than the other (*b*).



(III.)



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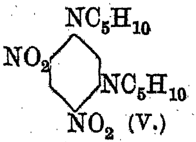
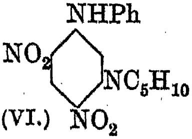


(V.)

The evidence for this assertion, apart from a very general reference to the work of " Nietzki and others " on the interaction of amines with this compound, consisted in the facts that ethyl sodio-malonate and -acetoacetate each reacted with only one chlorine atom, and that a second similar group was introduced only with difficulty. In the same paper there is described the compound (IV), and we therefore expected to find that the dichlorodinitrobenzene would, even under conditions sufficing to effect the conversion, *e.g.*, of 2 : 4-dichloronitrobenzene into 1-nitro-2 : 4-dipiperidinobenzene, give mainly (IV) and that the corresponding *dipiperidino*-compound (V) would be obtainable only with difficulty. Actually the reverse was the case. Borsche and Bahr's compound (IV) was certainly obtainable if care were exercised, but in presence of a slight excess of piperidine there occurred rapid formation of (V), which is very readily obtainable by warming the dichlorodinitrobenzene with enough piperidine to dissolve it. Moreover, the chlorine atom in (IV) is sufficiently mobile to react rapidly with aniline to give 4 : 6-*dinitro*-3-*anilino*-1-*piperidinobenzene* (VI).

Kenner (J., 1914, **105**, 2717) and Davies and Hickox (J., 1922, **121**, 2640) also have criticised some of Borsche's conclusions in connexion with other work on 1 : 3-dichloro-4 : 6-dinitrobenzene. Similarly, we are unable to agree with Hodgson (*J. Soc. Dyers and Col.*, 1926, 42) that the existence of two forms of 1-chloro-3-bromo-4 : 6-dinitrobenzene is capable of satisfactory explanation only by means of Borsche's conceptions, since at least six halogenonitrobenzenes, including 1 : 3-dibromo-4 : 6-dinitrobenzene (Jackson and Cohol, *Amer. Chem. J.*, 1903, **26**, 4), have been found to exhibit polymorphism.

1 : 3 : 5-Tribromo-2 : 4-dinitrobenzene is readily converted by two mols. of piperidine into a compound which we regard as 1 : 3-*dibromo*-2 : 4-*dinitro*-5-*piperidinobenzene* (VII), since (Borsche and Rantscheff, *Annalen*, 1911, **379**, 152) the halogen atom in 2-chloro-1 : 3-dinitrobenzene is less reactive than that in 1-chloro-2 : 4-dinitrobenzene. Excess of piperidine converts the original tribromo-compound with violence into 2 : 4-dinitro-1 : 3 : 5-tripiperidinobenzene (VIII), a compound obtained by Borsche and Trautner (*Annalen*, 1926, **447**, 1) from 1 : 3 : 5-trichloro-2 : 4-dinitrobenzene. These authors report the m. p. as 147—148°, but it actually melts 30° higher, and it is possible that this affords another illustration of the unsatisfactory nature of Borsche's method of using piperidine (see Experimental).



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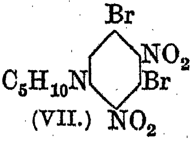
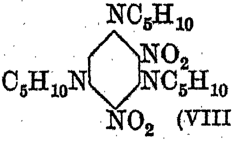


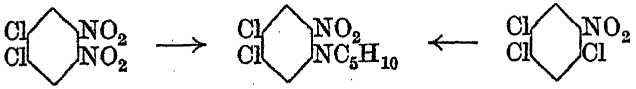
(VII.)



(VIII.)

The possibility of a reaction occurring owing to the activating effect of an ortho-para- on a meta-orienting substituent in the *m*-position to it, which has been observed in a few instances, *e.g.*, Tiemann (*Ber.*, 1891, **24**, 709), Kenner and others (J., since 1914), and Morgan (J., 1920, **117**, 784; 1921, **119**, 1537), has not been overlooked. It seems, however, that when there is no great crowding of groups, particularly nitro-groups, evidence based on the removal of halogen is trustworthy, *i.e.*, in general, only that halogen is labile which is in the *o*- or *p*-position to the nitro-group.

A reaction of piperidine with a compound having a labile nitro-group has been utilised to prove the constitution of the product obtained from 2 : 4 : 5-trichloro-1-nitrobenzene and piperidine.

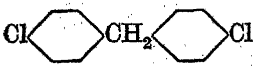


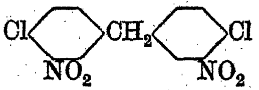
Thus, 1 : 2-dichloro-4 : 5-dinitrobenzene reacts readily with piperidine to give 4 : 5-dichloro-2-nitropiperidinobenzene, a nitro-group being replaced by a piperidino-group.

4 : 4′-Dichlorodiphenylmethane (IX) on nitration gave mainly 4 : 4′-*dichloro*-3 : 3′-*dinitrodiphenylmethane* (X), the constitution of which follows from its conversion, by piperidine, into 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylmethane.*

The nitration of 4 : 4′-dibromo-*s*-diphenylethane (XI) was far from quantitative, but a nitro-derivative was isolated with a m. p. ascribed in the literature to 4 : 4′-dibromo-? : ?-dinitro-*s*-diphenylethane, and therefore evidently the main, or most readily isolable, product of the nitration. Since piperidine converted this compound into a *dipiperidino*-compound, it is clearly 4 : 4′-*dibromo*-3 : 3′-*dinitro*-s-*diphenylethane* (XII).

(IX.)





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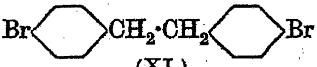
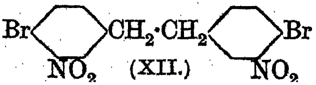


(XI.)



(XII.)

EXPERIMENTAL.

General Method of Preparation of Piperidino-derivatives.—Except where otherwise stated, these derivatives were prepared by gently boiling, for 3 minutes, the halogenonitro-compound with that amount of piperidine which effects complete solution. In cases where interaction was violent, a solvent such as alcohol was also used. As a rule, reaction was accompanied by the appearance of a bright red colour, the cooled product usually setting to a crystalline magma of piperidine hydrohalide. Water was added, and frequently solidification then ensued. Two methods of inducing crystallisation were particularly effective in cases of delayed solidification due to the presence of a trace of water or of unchanged halogen-compound: (*a*) The oily piperidino-derivative was dissolved in benzene, and the solution left over anhydrous sodium sulphate for a few minutes. Evaporation of the filtered solvent followed by desiccation in a vacuum, in most cases caused solidification. (*b*) In other cases, the oily derivative was warmed with dilute mineral acid, and the liquid was cooled, filtered, and basified. These two methods are referred to below as treatments (*a*) and (*b*) respectively.

3 : *3′-Dinitro-*4 : *4′-dipiperidinodiphenylsulphone* (II).—4 : 4′-Dichloro-3 : 3′-dinitrodiphenylsulphone gave a yellow coloration with cold piperidine and reacted violently with the latter on warming. The crude product was solid, was only slightly soluble in carbon tetrachloride, chloroform, benzene, or toluene, but was more soluble in acetone and methyl alcohol. It separated from methylated spirit in long, yellow needles, m. p. 183·5° (Found: N, 11·9. $C_{22}H_{26}O_6N_4S$ requires N, 11·8%).

4-*Bromo*-2-*nitropiperidinobenzene*.—The oily product of the interaction of 2 : 5-dibromonitrobenzene did not solidify after treatment (*a*), but did so after treatment (*b*). It separated from alcohol in deep red prisms, m. p. 48—49° (Found : Br, 28·1. $C_{11}H_{13}O_2N_2Br$ requires Br, 28·1%).

1-*Nitro*-2 : 4-*dipiperidinobenzene*.—The product of interaction of 2 : 4-dichloronitrobenzene and piperidine solidified after treatment (*a*). The crude piperidino-derivative was a mass of red-orange needles, m. p. 63—64°. When the solution in alcohol was cooled, there was a sudden deposition of radiating bunches of hexagonal leaflets, m. p. 67—68° (Found : N, 14·8. $C_{16}H_{23}O_2N_3$ requires N, 14·5%).

2-*Chloro*-4-*nitropiperidinobenzene*.—3 : 4-Dichloronitrobenzene and piperidine gave a yellow solution in the cold, and reacted vigorously on warming. Treatment (*b*) was necessary to induce solidification and then crystallisation from aqueous alcohol gave small, lemon-yellow plates, m. p. 47—48° (Found: N, 12·4; Cl, 14·9. $C_{11}H_{13}O_2N_2Cl$ requires N, 11·6; Cl, 14·8%).

4 : 5-*Dichloro*-1-*nitro*-2-*piperidinobenzene*.—2 : 4 : 5-Trichloronitrobenzene reacted with piperidine to give an oil which solidified only after treatment (*a*). It then separated from alcohol in red prisms, m. p. 64—65° (Found : Cl, 25·9. $C_{11}H_{12}O_2N_2Cl_2$ requires Cl, 25·8%).

5-*Nitro*-2-*piperidinobenzoic Acid and the Corresponding Ethyl Ester*.—*o*-Chlorobenzoic acid (55 g.) was added to 300 g. of nitric acid (*d* 1·5), and the resulting solution, after being left for 10 minutes, was poured on ice. The crude nitro-acid (42·5 g.) melted at 163—164°, whereas Hübner, for the pure acid, gives 165° (*Annalen*, 1884, **222**, 195).

The 2-chloro-5-nitrobenzoic acid reacted readily with piperidine to give the *piperidino-acid*, m. p. 201—202°, and when heated with alcohol and concentrated sulphuric acid gave the ethyl ester as a pale yellow oil, b. p. 190—191°/16 mm., solidifying at about 25°. Ethyl 2-chloro-5-nitrobenzoate reacted vigorously with piperidine without the application of heat. Treatment (*a*) led to the solidification of *ethyl* 5-*nitro*-2-*piperidinobenzoate*, which separated from aqueous alcohol in bright yellow, rectangular plates, m. p. 78—79° (Found: N, 10·2. $C_{14}H_{18}O_4N_2$ requires N, 10·1%).

3-*Nitro*-4-*piperidinobenzoic Acid*.—Addition of the diazo-solution prepared from *p*-chloroaniline (hydrochloric acid) to a solution of potassium cuprocyanide gave a 45% yield of almost pure *p*-chlorobenzonitrile. Nitration of the latter with nitric acid (*d* 1·5) at 5° gave a crude 4-chloro-3-nitrobenzonitrile, m. p. about 94°. Crystallisation from alcohol gave a product melting at 100—101°, as recorded by Claus and Kurz (*J. pr. Chem.*, 1888, **37**, 197), who obtained the nitrile from 4-chloro-3-nitroaniline by the diazo-process.

The nitrile was converted by piperidine into 3-nitro-4-piperidinobenzonitrile, m. p. 110—111° (compare Borsche, Stackmann, and Makaroff-Semljanski, *Ber.*, 1916, **49**, 2222), and by boiling 70% sulphuric acid into 4-chloro-3-nitrobenzoic acid. The latter reacted with piperidine quite as readily as did 2-chloro-5-nitrobenzoic acid, and the product (m. p. 202—203°) was evidently identical with that obtained by the last-mentioned authors by hydrolysing 3-nitro-4-piperidinobenzonitrile, the latter being obtained by them from 4-bromo-3-nitrobenzonitrile and piperidine.

Ethyl 3-*nitro*-4-*piperidinobenzoate* was obtained by esterification of the corresponding acid, with alcohol and sulphuric acid, as a red, viscous syrup (Found: N, 10·0. $C_{14}H_{18}O_4N_2$ requires N, 10·1%).

Behaviour of Piperidine towards o-*Chlorobenzoic Acid*.—(*a*) The acid was recovered unchanged after being heated for 6 hours with piperidine at the b. p. of the mixture. (*b*) The acid was heated with anhydrous potassium carbonate and piperidine in the presence of a little copper bronze. It was converted into salicylic acid.

4 : 6-*Dinitro*-1 : 3-*dipiperidinobenzene* (V).—Since 1 : 3-dichloro-4 : 6-dinitrobenzene reacted explosively in the cold, it was dissolved in pyridine and excess of piperidine added slowly, with external cooling. The dark brown, crystalline paste was filtered off; the solid so obtained separated from glacial acetic acid in dark yellow leaflets, m. p. 130—131° (Found: N, 16·9. $C_{16}H_{22}O_4N_4$ requires N, 16·8%).

3-*Chloro*-4 : 6-*dinitropiperidinobenzene* (IV).—A solution of 3·6 g. of piperidine in 15 c.c. of alcohol was added, slowly and with shaking, to a solution of 4 g. of 1 : 3-dichloro-4 : 6-dinitrobenzene in 50 c.c. of alcohol. The mixture was gently boiled for 10 minutes and then diluted with water, and the resulting yellow product was washed and crystallised thrice from alcohol. It then had m. p. 119° (compare Borsche and Bahr, *loc. cit.*).

4 : 6-*Dinitro*-3-*anilino*-1-*piperidinobenzene* (VI).—The previous

compound was heated with excess of aniline for 3 minutes, and the cooled solution was then poured into excess of dilute hydrochloric acid. The resulting black, brittle, solid product, after two crystallisations from glacial acetic acid, formed bright yellowish-green plates, m. p. 148—148·5° (Found : N, 16·6. $C_{17}H_{18}O_4N_4$ requires N, 16·4%).

Action of Piperidine on 1 : 3 : 5-*Tribromo*-2 : 4-*dinitrobenzene.*—(*a*) To a solution of 4 g. (1 mol.) of tribromodinitrobenzene in 25 c.c. of boiling chloroform were added 2·2 c.c. (2·25 mols.) of piperidine dissolved in 10 c.c. of chloroform. The solution was then boiled for a further 2 minutes, the chloroform removed by evaporation, and the residue extracted with water. The residue, on crystallisation from alcohol, gave 1 : 3-*dibromo*-2 : 4-*dinitro*-5-*piperidinobenzene* (VII) in yellow plates, m. p. 125—126° (Found: Br, 39·0. $C_{11}H_{11}O_4N_3Br_2$ requires Br, 39·1%).

(*b*) With 4·3 c.c. of piperidine and 4 g. of the tribromo-compound, under the above conditions, a mixture was obtained.

(*c*) When the tribromo-compound was treated with excess of piperidine a violent reaction at once set in, and even with careful cooling it was found difficult to prevent some *actual charring* in the centres of the masses formed. Addition of water, filtration, and crystallisation from alcohol led to yellow needles of 2 : 4-dinitro-1 : 3 : 5-tripiperidinobenzene (VIII), m. p. 177—178° (Found: N, 16·5. $C_{21}H_{31}O_4N_5$ requires N, 16·8%).

1 : 2-*Dichloro*-4 : 5-*dinitrobenzene.*—The preparation of this substance from *o*-dichlorobenzene by the method described by Hartley and Cohen (J., 1904, **85**, 867) is very tedious, since even after two lengthy nitration processes the product is a mixture. We have found it more convenient to nitrate *o*-dichlorobenzene, separate the 3 : 4-isomeride—a comparatively simple matter—and nitrate it. 3 : 4-Dichloronitrobenzene (10 g.) was dissolved in 60 c.c. of nitric acid (*d* 1·5), and 40 c.c. of fuming sulphuric acid (20% SO_3) were added. The solution was heated for 2 hours at 100°, then cooled and poured into water. The solid precipitated, after being twice crystallised from dilute acetic acid, gave the dinitro-compound, m. p. 109—110° (Hartley and Cohen give 104°; Nietzki and Konwaldt, *Ber.*, 1904, **37**, 3892, give 114°).

Action of Piperidine on 1 : 2-*Dichloro*-4 : 5-*dinitrobenzene.*—This chloronitro-compound reacted in the cold with piperidine. The reaction was completed by boiling for a few minutes, and the resulting solution was treated with water. The red oil precipitated was washed with very dilute hydrochloric acid and then with water. Crystals, m. p. 62—64°, separated on inoculation of an alcoholic solution with solid obtained as above from trichloronitrobenzene.

The two products were identical. The unidirectional nature of the reaction just described is perhaps worth comment. Aniline and other primary bases give products which are much less easily isolated.

4 : 4′-*Dichlorodiphenylmethane*.—Montagne (*Rec. trav. chim.*, 1906, **25**, 390, 412) had previously obtained this substance by reducing 4 : 4′-dichlorobenzophenone, but we have obtained it more conveniently as follows: 4 : 4′-Diaminodiphenylmethane (25 g.) was dissolved in 150 c.c. of concentrated hydrochloric acid with the addition of 150 c.c. of water. The suspension (obtained on cooling) was diazotised with 17 g. of sodium nitrite dissolved in 40 c.c. of water, ice being added at intervals to keep the temperature at 0°. The resulting clear solution (about 600 c.c.) was poured into a cooled solution of cuprous chloride in hydrochloric acid (made from 150 g. of copper sulphate pentahydrate). A biscuit-coloured copper compound separated, which decomposed when the mixture was warmed at 100° for 0·5 hour. The brown oil formed was extracted with benzene, and isolated by distillation under reduced pressure; 15 g. of dichloro-compound, b. p. 186—190°/18 mm., m. p. 55—56° (after one crystallisation from alcohol), were then obtained.

4 : 4′-*Dichloro*-3 : 3′-*dinitrodiphenylmethane* (X).—The dichloro-compound was added to eight times its weight of water-cooled nitric acid (*d* 1·5). After a few minutes, when crystals began to separate, the mixture was poured into excess of water. The precipitated solid was slightly soluble in light petroleum (b. p. 80—100°) and in acetone, but more soluble in benzene, chloroform, and alcohol. It separated from glacial acetic acid in white plates, m. p. 198—199° (Found: Cl, 21·6. $C_{13}H_8O_4N_2Cl_2$ requires Cl, 21·7%).

The dinitro-compound reacted normally with piperidine to give 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylmethane*, which, after being crystallised first from glacial acetic acid and then from alcohol, melted at 183—184° (Found: N, 13·4. $C_{23}H_{28}O_4N_4$ requires N, 13·2%).

4 : 4′-*Dibromo*-3 : 3′-*dinitro*-s-*diphenylethane* (XII).—4 : 4′-Dibromo-*s*-diphenylethane, m. p. 114°, prepared by the direct bromination of *s*-diphenylethane (compare Stelling and Fittig, *Annalen*, 1866, **137**, 267) was added to 15 parts of water-cooled nitric acid (*d* 1·5). The solution was warmed gently for 15 minutes, cooled, and poured into water. The resulting gummy precipitate, when dry, separated from benzene with m. p. 155—160°. Two further crystallisations gave small, yellowish-white crystals, m. p. 204°, the figure given by Stelling and Fittig.

The dinitro-compound was converted by piperidine into a product which separated from glacial acetic acid in orange-yellow, microscopic needles, m. p. 235—240°, with previous shrinking (Found: N, 13·0. $C_{24}H_{30}O_4N_4$ requires N, 12·8%).

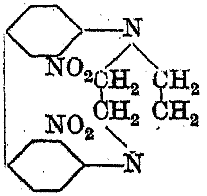
The Use of Sodium Acetate in the Preparation of Piperidino-compounds.—Borsche and his co-workers (*loc. cit.*) prepared a number of piperidino-compounds by heating 1 mol. of halogenonitro-compound with 1 mol. of piperidine hydrochloride (per 1 atom of reactive halogen) and excess of sodium acetate in alcoholic solution. Using this method with *p*-chloronitrobenzene, only a 36% yield has been obtained by us, whereas with 2·5 mols. of piperidine at 100°, almost theoretical conversion is effected.

Again, 4-chloro-3-nitrobenzonitrile gave only a 40% yield of piperidino-compound by Borsche's method, whilst almost theoretical yields were obtained by using piperidine alone at 100°.

1 : 4-*Di*-op-*dinitrophenylpiperazine.*—Piperazine (1 mol. of the hexahydrate) was heated with 3 mols. of 1-chloro-2 : 4-dinitrobenzene. At the b. p. of the mixture, sudden interaction occurred, and the previous two layers became an orange paste. After extraction with boiling alcohol and hot water, a product remained which was sparingly soluble in hot or cold glacial acetic acid, pyridine, acetone, or chloroform. It separated from nitrobenzene in orange-red needles, decomp. with effervescence at about 240° (Found: N, 20·3. $C_{16}H_{14}O_8N_6$ requires N, 20·1%).

1 : 4-*Di*-oop-*trinitrophenylpiperazine* (1 : 4-*dipicrylpiperazine*), prepared similarly, crystallised from nitrobenzene in orange needles, not melting at 260° (Found : N, 22·2. $C_{16}H_{12}O_{12}N_8$ requires N, 22·0%).

Interaction of Piperazine with 4 : 4′-Dibromo-3 : 3′-dinitrodiphenyl.—These two substances might conceivably interact to give a compound of the following structure (see, however, Le Fèvre and Turner, J., 1926, 2476) :



A solution of 1 g. of dibromodinitrodiphenyl and 0·5 g. of piperazine hexahydrate in 30 c.c. of pyridine was boiled for 2 hours, and then evaporated to a small bulk. The reddish-orange *powder* which separated on cooling, after crystallisation from pyridine, melted at about 215° (Found : N, 14·0. $C_{16}H_{15}O_4N_4Br$ requires N, 13·8%).

The substitution of benzidine for piperazine in the last experiment gave brown *needles*, from pyridine, m. p. 251° (Found : N, 10·8. $C_{24}H_{17}O_4N_4Br$ requires N, 11·1%).

In neither case, therefore, is a " Kaufler " compound formed.

One of us (R. J. W. Le F.) has pleasure in acknowledging a maintenance grant from the Department of Scientific and Industrial Research, and also a grant allocated to him by the Research Grant Committee of the Chemical Society.

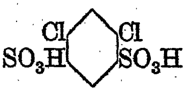
East London College,
University of London.

[*Received, March* 12*th*, 1927.]

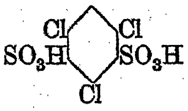
CLIII.—*The Disulphonation of* m-*Dichlorobenzene and of* s-*Trichlorobenzene.*

By William Davies and Harry Gordon Poole.

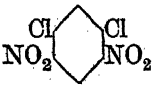
When this investigation was begun it was hoped that the chlorine atoms in (I) and (II) would be very reactive, as they are in (III) (compare Davies and Hickox, J., 1922, **121**, 2640), and would lend themselves to similar condensations. The easy elimination of the sulphonic groups from the condensation products would then give mixed aromatic–aliphatic compounds of some synthetic importance. The chlorine atoms in (I) and (II) are, however, practically non-reactive compared with those in (III), and the contemplated condensations could not be brought about.



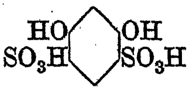
(I.)



(II.)



(III.)



(IV.)

The disulphonic acid formed by the direct sulphonation of *m*-dichlorobenzene gives a sulphonyl chloride identical with that already prepared by the action of phosphorus pentachloride on salts of (IV) (Pollak and Wienerberger, *Monatsh.*, 1914, **35**, 1472). Hence the constitution (I) is justified. Nothing was previously known of the disulphonic acid of *s*-trichlorobenzene, which must, however, have the formula indicated (II). Both *m*-dichlorobenzene and *s*-trichlorobenzene are much less readily sulphonated than the corresponding methyl derivatives of benzene, despite the fact that the chlorine atom is considered to have a greater directive power than the methyl group (Holleman, *Chem. Reviews*, 1924—1925, I, 2, 202).

Experimental.

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonic Acid.*—*m*-Dichlorobenzene (30 g.) is dropped with cooling into fuming sulphuric acid (70 c.c.; 45% SO$_3$), and the mixture heated at 140—150° for 5 hours. The product after cooling and treatment with ice is converted into the

barium salt, and this into the sulphonyl chloride by heating it with phosphorus pentachloride at 130—140° for 6 hours. The sulphonyl chloride crystallises from petroleum (b. p. 100—120°) in large, thick rhombohedra, and also less frequently in long, thin needles, both forms melting at 122—123° (Pollak and Wienerberger, *loc. cit.*, record m. p. 122—123°). The crystals provide an excellent example of triboluminescence, the flashes being sufficiently brilliant to be seen in ordinary electric light (Found: C, 20·7; H, 0·9. Calc.: C, 20·9; H, 0·6%).

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonic acid* forms plates very soluble in water, and can be crystallised from concentrated sulphuric acid. The *amide*, colourless needles, m. p. 276°, is readily soluble in hot and sparingly soluble in cold water. The sodium and the barium salt are very soluble in cold water, but the *potassium* salt is very soluble in hot and only moderately easily soluble in cold water, from which it separates in colourless prisms (Found in the air-dried salt: H_2O, 1·25. $C_6H_2O_6Cl_2S_2K_2,\frac{1}{4}H_2O$ requires H_2O, 1·2. Found in anhydrous salt: K, 20·3. $C_6H_2O_6Cl_2S_2K_2$ requires K, 20·4%). When the potassium salt is boiled for 24 hours with excess of aqueous-alcoholic potassium hydroxide, the quantity of chlorine displaced is less than 0·5% of that calculated for the displacement of one atom of chlorine. Bromine water attacks the salts or the acid extremely slowly, in marked contrast to the action with *m*-xylene-4 : 6-disulphonic acid.

s-*Trichlorobenzenedisulphonic Acid.*—2 : 4 : 6-Trichloroaniline has hitherto been prepared by passing chlorine into a solution of aniline in chloroform (Meyer and Sudborough, *Ber.*, 1894, **27**, 3151; Willgerodt and Wilcke, *Ber.*, 1910, **43**, 2747). This process produces large quantities of mono- and di-chloroanilines, the formation of which is hindered in the following method. Aniline (100 g.) is added drop by drop to a cold solution of chlorine (160 g.) in carbon tetrachloride (1000 g.). During the reaction a good stream of chlorine is passed, and excess of chlorine maintained. It is essential to keep the reaction mixture cold during the experiment, which requires about 5 hours. The product is worked up after the method of Willgerodt and Wilcke (*loc. cit.*); the yield of trichloroaniline is 120 g. (W. and W. obtained 78 g.). The conversion of trichloroaniline into *s*-trichlorobenzene by the method of Jackson and Lamar (*J. Amer. Chem. Soc.*, 1896, **18**, 667) gives an excellent yield. The yield is increased by treating the residue with 70% sulphuric acid, in the usual way, to remove aniline.

s-Trichlorobenzene is recovered unchanged after being heated with concentrated sulphuric acid at 100° for 56 hours, and is only partly sulphonated when heated at this temperature with fuming sulphuric acid (12% SO_3) for 6 hours. But when *s*-trichlorobenzene (9 g.) is heated on the water-bath with fuming sulphuric acid (25 c.c.; 72% SO_3) for 15 hours, complete disulphonation occurs. Disulphonation also takes place with this strength of acid in 5 hours at 115—120°, but the product is not so pure as that obtained at the lower temperature. The dry sodium salt (17 g.) is prepared *via* the calcium or barium sulphonate in the usual way, and when heated for 3 hours with three times its weight of phosphorus pentachloride and a little phosphorus oxychloride, is smoothly converted into the sulphonyl chloride (70% yield of the pure product). s-*Trichlorobenzenedisulphonyl chloride* crystallises from petroleum (b. p. 100—120°) or ethyl acetate in prisms, m. p. 161·5° (Found: Cl, 47·1; S, 16·6. $C_6HO_4Cl_5S_2$ requires Cl, 46·8; S, 16·9%). Owing to the high melting point of the sulphonyl chloride the *amide* cannot be easily obtained by the action of aqueous ammonia in the usual way; it is formed, however, by the addition of concentrated aqueous ammonia to the sulphonyl chloride in benzene. It is readily soluble in boiling and sparingly soluble in cold water, from which it separates in minute, colourless needles, m. p. 248° (Found: N, 8·5. $C_6H_5O_4N_2Cl_3S_2$ requires N, 8·3%).

s-*Trichlorobenzenedisulphonic acid* separates from concentrated sulphuric acid, in which it is moderately easily soluble, in colourless needles very soluble in water. The normal *sodium* salt is extremely soluble in water, and the normal *barium* salt (needles) dissolves in about its own weight of water at the ordinary temperature, but both salts are sparingly soluble in absolute alcohol. The *potassium* salt is slightly soluble in boiling and sparingly soluble in cold water, from which it crystallises in small, compact prisms (Found in air-dried material: H_2O, 0·1%. Found in anhydrous salt: K, 18·6. $C_6HO_6Cl_3S_2K_2$ requires K, 18·7%). Prolonged treatment of the potassium salt with boiling potassium hydroxide solution produces only a trace of potassium chloride, showing that the chlorine atoms are not reactive under the particular conditions investigated.

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[*Received, March 15th,* 1927.]

CLIV.—*Some Experiments with* 1 : 8-*Naphthalyl Chloride.*

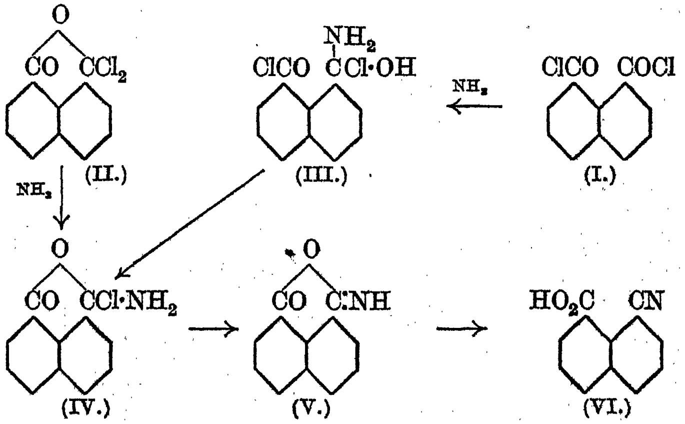
By WILLIAM DAVIES and GEOFFREY WINTHROP LEEPER.

IT is known that the dichlorides of several dicarboxylic acids (*e.g.*, *o*-phthalic acid) can exist in two tautomeric forms and it was therefore decided to examine 1 : 8-naphthalyl chloride (Mason, J., 1924,

125, 2116) in order to determine whether an analogous type of tautomerism could occur in this case; the examination, however, has failed to reveal the existence of more than one form, both distillation under 0·2 mm. pressure and treatment with aluminium chloride leaving the chloride unchanged.

Catalytic reduction of the chloride by Rosenmund's method (*Ber.*, 1921, **54**, 432) under conditions which gave an excellent yield of benzaldehyde from benzoyl chloride gave a complex mixture from which only naphthalic anhydride could be isolated.

The interactions of naphthalyl chloride and of phthalyl chloride with ammonia follow similar courses, but the production of 1-cyano-8-naphthoic acid can be explained equally well by either of the possible formulæ for naphthalyl chloride (I) or (II) *via* the intermediate compounds (III), (IV), and (V) (compare Staudinger, *Ber.*, 1911, **44**, 1643). It is noteworthy, however, that ammonia reacts very slowly with the chloride in benzene solution.



The action of aniline and of dimethylaniline on naphthalyl chloride followed normal lines, yielding, respectively, 1 : 8-naphthaldianilide and 1 : 8-naphthalbisdimethylanilide.

The evidence obtained therefore leaves the question of the constitution of 1 : 8-naphthalyl chloride still unsettled.

EXPERIMENTAL.

1 : 8-Naphthalyl chloride was prepared after the method of Mason (*loc. cit.*). It is advantageous to use glacial phosphoric acid as grease for the ground joint in the bromine flask in order to prevent seizing. In addition to the properties already described, naphthalyl chloride is very soluble in benzene, hot or cold. Attempts to distil it under moderately reduced pressure lead to complete decomposition

as mentioned by Mason, some carbonyl chloride being produced. The substance, however, distils unchanged at 195—200°/about 0·2 mm. when the operation is rapidly carried out on small quantities (about 10 g.).

Attempted Conversion into the Tautomeric Form.—When the acid chloride is heated for several hours with its own weight of powdered aluminium chloride in a sealed tube, no appreciable change occurs at about 86°, and complete decomposition takes place at about 115°. Since the substance can even be distilled without the other tautomeric form being produced, it is evident that the acid chloride has no great tendency to exhibit tautomerism.

1-*Cyano*-8-*naphthoic Acid.*—A solution of naphthalyl chloride (10 g.) in benzene (150 c.c.) is filtered from a trace of anhydride, and a stream of dry ammonia passed into it for 2 hours with shaking and occasional heating. Reaction readily occurs and a copious grey precipitate is formed. The benzene filtrate smells strongly of ammonia, but evolves a large quantity of hydrogen chloride after 12 hours. This phenomenon is also observed when the ammonia has been passed for a much longer period, and seems to indicate that the acid chloride is not very reactive towards dry ammonia. Concentrated aqueous ammonia and a benzene solution of the acid chloride rapidly interact, but the product is naphthalic anhydride. The above-mentioned grey precipitate is collected and shaken with hot aqueous sodium carbonate, the filtered red solution is quickly cooled and acidified with acetic acid, and the naphthalic acid produced is collected; the filtrate is then strongly acidified with hydrochloric acid, whereupon about 3 g. of the crude *cyanonaphthoic acid* separate. It crystallises from benzene–light petroleum, or from nitrobenzene, in clusters of colourless needles. It is sparingly soluble in water, moderately easily soluble in most of the usual organic solvents, and melts indefinitely with decomposition at 210—250°; the product contains naphthalimide, m. p. 300° (Found: equiv., 196·8; N, 7·1. $C_{12}H_7O_2N$ requires equiv., 197; N, 7·1%).

Cyanonaphthoic acid is very reactive. It dissolves in cold concentrated sulphuric acid with a purple fluorescence, and is gradually converted into naphthalic anhydride (m. p. 274°; mixed m. p. 274°). It dissolves readily in cold dilute sodium hydroxide solution and in warm ammonia and sodium carbonate solutions, from which it is only partly precipitated by excess of acetic acid, but completely by mineral acid. The solution in any of the alkaline reagents mentioned, when boiled for some time, deposits a large amount of crystalline matter in the heat, and the cyanonaphthoic acid is rapidly destroyed. Probably salts of naphthalic acid and of the acid amide of naphthalic acid are produced. Attempts to methylate the cyanonaphthoic acid with silver oxide and methyl iodide gave methyl naphthalate, m. p. 102° (mixed m. p. 102°).

1 : 8-*Naphthaldianilide.*—A dilute benzene solution of naphthalyl chloride is mixed with excess of aniline in benzene and the solid which slowly settles is collected after 24 hours. This is well washed with benzene and repeatedly with boiling water, and the dried substance is crystallised from nitrobenzene, from which it separates in minute, colourless needles melting with decomposition at 250—282° according to the rate of heating (Found : N, 7·9. $C_{24}H_{18}O_2N_2$ requires N, 7·65%). The substance is only sparingly soluble in low-boiling organic solvents.

1 : 8-*Naphthalbisdimethylanilide* is formed similarly, but in this case a large quantity of naphthalic anhydride is formed, which is removed by repeated extraction with boiling potassium hydroxide solution. 1 : 8-*Naphthalbisdimethylanilide* separates from nitrobenzene in minute prisms, melting sharply at 245—246° without decomposition (Found : N, 7·4. $C_{26}H_{22}O_2N_2$ requires N, 7·2%).

The authors wish to record their indebtedness to Dr. F. A. Mason and Mr. L. Rubenstein for advice and assistance in the preparation of naphthalyl chloride. One of them (W. D.) also wishes gratefully to acknowledge grants from the Research Fund Committee of the Chemical Society and the Government Grant Committee of the Royal Society, and a Senior Studentship from the Commissioners of the 1851 Exhibition, which have all been partly applied to the prosecution of the above work.

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[*Received, March* 15*th*, 1927.]

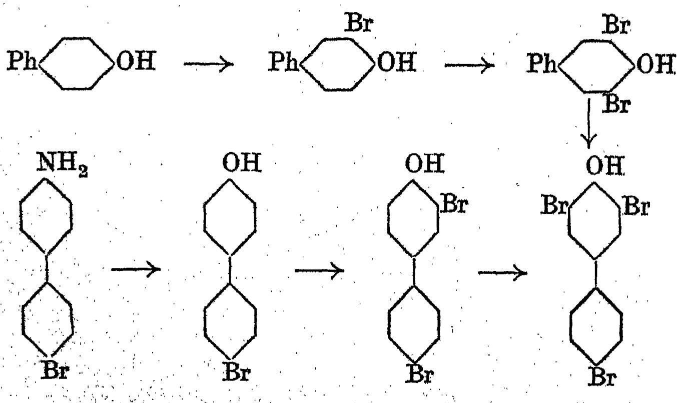
CLV.—*Investigations in the Diphenyl Series. Part V. Derivatives of 4-Amino- and 4-Hydroxy-diphenyl.*

By FRANK BELL and PERCY HARRY ROBINSON.

SINCE dinitro-4-methylaminodiphenyl (Bell and Kenyon, J., 1926, 2711) is resistant to acetylating agents, it was inferred that the nitro-groups are in the 3 : 5-positions. This view is substantiated by the fact that 3-nitro-4-methylaminodiphenyl is readily acetylated. 3-Nitro-4-methylaminodiphenyl, which had previously been obtained by the oxidation of 3-nitro-4-dimethylaminodiphenyl (Garciá Banús and Ferrer Tomás, *Anal. Fis. Quim.*, 1921, **19**, 293), was advantageously prepared by the hydrolysis of 3-*nitro*-4-p-*toluenesulphonmethylamidodiphenyl*, obtained by nitration of the corresponding amide. It appears that the orienting influence of the *p*-toluenesulphonmethylamido-group is very similar to that of the acetamido-group. This conclusion is supported by a comparison of the results of the nitration of *p*-toluenesulphonmethylanilide with that of acetanilide, since the ratio of *p* : *o* substitution is very approximately the same in both cases.

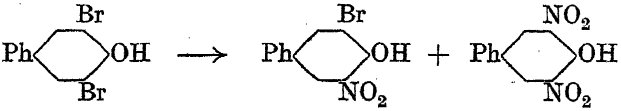
The further substitution of 3 : 4-derivatives of diphenyl is of considerable interest. On further nitration, 3-nitro-4-acetamido-(or dimethylamino-)diphenyl and 3-nitro-4-hydroxydiphenyl yield only 5-nitro-derivatives (Fichter and Sulzberger, *Ber.*, 1904, **37**, 878; Bell and Kenyon, *loc. cit.*; Garciá Banús and Guiteras, *Anal. Fis. Quim.*, 1923, **21**, 126), but 3-nitro-4-methoxydiphenyl, in addition, gives about 15% of the 4′-nitro-derivative (Bell and Kenyon, J., 1926, 3046). The somewhat surprising production of the 4′-bromo-derivative in the bromination of 4-acetamidodiphenyl (Scarborough and Waters, J., 1926, 558; Kenyon and Robinson, *ibid.*, p. 3050) suggested that the bromination of the above compounds might yield interesting results, and 3-nitro-4-acetamidodiphenyl has now been examined. The product consists mainly of the 5-bromo-derivative, together with some of the 5 : 4′-dibromo-derivative and small amounts of other products. No 4′-bromo-3-nitro-4-acetamidodiphenyl was isolated from the reaction mixture.

The bromination of 4-hydroxydiphenyl has now been shown to follow a normal course. Monobromination gives the 3-derivative, dibromination the 3 : 5-derivative, and tribromination the 3 : 5 : 4′-derivative. 4′-Bromo-4-hydroxydiphenyl was prepared from 4′-bromo-4-aminodiphenyl, and converted successively into 3′: 4′-dibromo- and 3 : 5 : 4′-tribromo-4-hydroxydiphenyl.



3 : 5-Dibromo-4-hydroxydiphenyl readily reacts with nitrous acid to give a complex mixture from which 5-bromo-3-nitro- and 3 : 5-

dinitro-4-hydroxydiphenyl have been isolated. This result is in marked contrast with that obtained by Raiford and Colbert (*J. Amer. Chem. Soc.*, 1925, 47, 1456), who not only failed to isolate these products, but stated that the principal product is a nitrodibromophenol, m. p. 171°. Of this, we can discover no trace.



EXPERIMENTAL.

Nitration of p-*Toluenesulphonmethylanilide.*—10 G. were added to warm nitric acid (20 c.c.); vigorous reaction then occurred. The cooled mixture was filtered from an insoluble part (8·5 g.), and the filtrate poured into water. The precipitated gum (1·3 g.) crystallised from alcohol in prismatic needles, m. p. 126°, identical with *p*-toluenesulphonmethyl-2-nitroanilide (described below). The less soluble material was crystallised from alcohol, and separated into *p*-toluenesulphonmethyl-4-nitroanilide, m. p. 175—176° (identified by comparison with a specimen prepared from *p*-nitroaniline and by hydrolysis to 4-nitromonomethylaniline), and a further small crop of the 2-nitro-derivative.

p-*Toluenesulphon-2-nitroanilide*, prepared by the interaction of *o*-nitroaniline and *p*-toluenesulphonyl chloride in pyridine solution, crystallised from alcohol in prismatic needles, m. p. 110° (Found: C, 54·1; H, 4·2. $C_{13}H_{12}O_4N_2S$ requires C, 53·4; H, 4·1%). By methylation with methyl sulphate it gave p-*toluenesulphonmethyl-2-nitroanilide*, m. p. 126° (Found: C, 54·4; H, 4·5. $C_{14}H_{14}O_4N_2S$ requires C, 54·9; H, 4·6%).

Nitration of 4-p-*Toluenesulphonmethylamidodiphenyl.*—To 12·5 g., dissolved in acetic acid (125 c.c.) at 70°, was added nitric acid (*d* 1·5; 10 c.c.) in acetic acid (10 c.c.), and the whole was maintained at 70—75° for ¼ hour. On cooling, the liquid became filled with needles (11 g., m. p. 154—156°), which were filtered off and, after recrystallisation from acetic acid, had m. p. 157° (Found: C, 63·2; H, 4·9. $C_{20}H_{18}O_4N_2S$ requires C, 62·8; H, 4·7%). The filtrate, when poured into water, gave gummy material (4·5 g.). The main product of the reaction was identical with 3-*nitro*-4-p-*toluenesulphonmethylamidodiphenyl*, prepared by the methylation of 3-nitro-4-*p*-toluenesulphonamidodiphenyl.

3-*Nitro*-4-*methylaminodiphenyl.*—A solution of 3-nitro-4-*p*-toluenesulphonmethylamidodiphenyl (10 g.) in sulphuric acid (20 c.c.) was after ½ hour poured on ice and neutralised with ammonia, and the resulting precipitate was filtered off and crystallised from alcohol. 3-Nitro-4-methylaminodiphenyl forms orange-red needles, m. p. 112°.

3-*Nitro-4-nitrosomethylaminodiphenyl*, prepared by the addition of a slight excess of sodium nitrite to a solution of 3-nitro-4-methylaminodiphenyl in acetic acid (10 parts), crystallised from alcohol in pale yellow needles, m. p. 87° (Found: C, 60·8; H, 4·4. $C_{13}H_{11}O_3N_3$ requires C, 60·7; H, 4·2%). Nitration converted it into 3 : 5-dinitro-4-nitrosomethylaminodiphenyl.

3-*Nitro-4-acetmethylamidodiphenyl*.—3-Nitro-4-methylaminodiphenyl was warmed on a water-bath with acetic anhydride, until the deep red colour of the solution faded to pale yellow. The solution was poured into water, and the gummy deposit dissolved in alcohol, from which it separated as a pale yellow, crystalline powder, m. p. 89° (Found: C, 66·8; H, 4·7. $C_{15}H_{14}O_3N_2$ requires C, 66·6; H, 5·2%).

Nitration of 4 : 4′-*Di*-p-*toluenesulphonamidodiphenyl*.—This compound (10 g.) was added slowly to nitric acid (*d* 1·4; 20 c.c.), and the mixture was diluted with acetic acid and filtered. 3 : 3′-*Dinitro*-4 : 4′-*di*-p-*toluenesulphonamidodiphenyl* crystallises from pyridine–ethyl alcohol in needles, m. p. 220° (Found: C, 53·8; H, 3·8. $C_{26}H_{22}O_8N_4S_2$ requires C, 53·6; H, 3·8%). It was hydrolysed by dissolving it in sulphuric acid (3 parts) and, after ½ hour, pouring the solution into water. Pure 3 : 3′-dinitrobenzidine, m. p. 275°, was obtained when the product was crystallised from pyridine–ethyl alcohol.

Bromination of 3-*Nitro-4-acetamidodiphenyl*.—To a solution of 3-nitro-4-acetamidodiphenyl (17 g.) in acetic acid (70 c.c.), bromine (11 g.) in acetic acid (5 c.c.), and ferric chloride (1 g.) were added. The mixture was heated on a water-bath for 10 hours, cooled, and filtered from a deposit (13 g.) which consisted mainly of the hydrobromides of bases produced by hydrolysis. The filtrate was poured into water; the gummy deposit (8 g.) thus obtained crystallised from alcohol in needles, m. p. 93—95° (Found: C, 50·4; H, 3·0. $C_{14}H_{11}O_3N_2Br$ requires C, 50·2; H, 3·3%). The hydrobromides were decomposed by boiling water and the mixture of amines obtained was acetylated. The acetyl derivatives were readily separated by crystallisation from alcohol into a less soluble portion, m. p. 140—150°, and a more soluble portion, m. p. 85—95°. The former, after crystallisation from carbon tetrachloride and then from alcohol, formed long, yellow needles, m. p. 153° (Found: C, 40·0; H, 2·4. $C_{14}H_{10}O_3N_2Br_2$ requires C, 40·5; H, 2·4%), whilst the latter, after repeated crystallisation, gave pure (5?)-*bromo*-3-*nitro-4-acetamidodiphenyl*, m. p. 94—95°. The compound, m. p.

153°, is probably 5 : 4′-*dibromo*-3-*nitro*-4-*acetamidodiphenyl*, since it was also obtained by the bromination of 4′-bromo-3-nitro-4-acetamidodiphenyl as follows. To a hot solution of 4′-bromo-4-acetamidodiphenyl (3 g.) in acetic acid (30 c.c.) was added nitric acid (*d* 1·5; 2 c.c.) in acetic acid (2 c.c.). After ½ hour, the mixture was allowed to cool; 4′-bromo-3-nitro-4-acetamidodiphenyl, m. p. 197—200°, then separated. This compound (2·4 g.), acetic acid (30 c.c.), bromine (1·6 g.), and ferric chloride were warmed together until hydrogen bromide ceased to be evolved. On cooling, the liquid filled with orange needles, m. p. 151—153°.

In addition to the 5- and 5 : 4′-bromo-derivatives, there was isolated a trace of a compound which crystallised from alcohol in colourless needles, m. p. 210—213° (Found: C, 45·6; H, 3·1; N, 3·8%).

4′-*Bromo*-4-*aminodiphenyl* was prepared by Le Fèvre and Turner's method (J., 1926, 2045) and characterised by means of its p-*toluenesulphonyl* derivative, which crystallised from alcohol in needles, m. p. 174° (Found: C, 57·2; H, 3·65. $C_{19}H_{16}O_2NBrS$ requires C, 56·7; H, 4·0%).

4′-*Bromo*-4-*hydroxydiphenyl*.—4′-Bromo-4-aminodiphenyl (10 g.) was dissolved in boiling dilute hydrochloric acid (700 c.c. of 1%), the solution rapidly cooled to 5—10°, and sodium nitrite (3 g.) added. After ½ hour, the solution was filtered, dilute sulphuric acid added, and steam passed in. The precipitate which formed was filtered off and extracted with boiling dilute aqueous sodium hydroxide. The extract was acidified with hydrochloric acid and the crude bromophenol precipitated was filtered off and crystallised from alcohol. 4′-*Bromo*-4-*hydroxydiphenyl* forms plates, m. p. 164—166° (Found: C, 57·6; H, 3·8. $C_{12}H_9OBr$ requires C, 57·8; H, 3·6%).

3 : 4′-*Dibromo*-4-*hydroxydiphenyl*.—To a warm solution of 4′-bromo-4-hydroxydiphenyl (10 g.) in chloroform (90 c.c.) was added bromine (6·5 g.) in chloroform (10 c.c.). The chloroform solution was evaporated to a small bulk and then diluted with light petroleum. On cooling, hard, stellate masses, m. p. 117°, were formed (Found: C, 44·2; H, 2·7. $C_{12}H_8OBr_2$ requires C, 43·9; H, 2·4%).

3 : 5 : 4′-*Tribromo*-4-*hydroxydiphenyl*, prepared as described above from 4′-bromo-4-hydroxydiphenyl (7·4 g.) and bromine (10·8 g.), crystallised from chloroform in stout needles, m. p. 159° (Found: C, 35·8; H, 1·9. $C_{12}H_7OBr_3$ requires C, 35·4; H, 1·7%).

3 : 4′-*Dibromo*-5-*nitro*-4-*hydroxydiphenyl*.—To a warm solution of 3 : 4′-dibromo-4-hydroxydiphenyl (3·2 g.) in acetic acid (20 c.c.) was added nitric acid (*d* 1·4; 0·8 c.c.) in acetic acid (10 c.c.). The

solution rapidly filled with small needles; these, after crystallisation from chloroform, had m. p. 189° (Found: C, 38·9; H, 2·0. $C_{12}H_7O_3NBr_2$ requires C, 38·6; H, 1·9%).

3-*Bromo*-4-*hydroxydiphenyl*.—To a warm solution of 4-hydroxydiphenyl (7·8 g.) in chloroform (70 c.c.) was added bromine (7·4 g.) in chloroform (10 c.c.). After partial evaporation of the chloroform, and dilution with light petroleum, the liquid filled with needles of 3-*bromo*-4-*hydroxydiphenyl*, m. p. 96° (Found: C, 57·8; H, 3·5. $C_{12}H_9OBr$ requires C, 57·8; H, 3·6%).

3 : 5-Dibromo-4-hydroxydiphenyl, obtained in quantitative yield by using 14·8 g. of bromine in the previous preparation, crystallised from chloroform–light petroleum in needles, m. p. 91—94° (Raiford gives m. p. 96°).

Oxidation of 4 g. with alkaline permanganate gave a trace of *p*-bromobenzoic acid, and we were unable to eliminate the small amount of impurity which gives rise to this acid. The dibromophenol is, however, readily characterised as its p-*toluenesulphonyl* derivative, which crystallises from acetic acid in needles, m. p. 132° (Found: C, 47·5; H, 2·6. $C_{19}H_{14}O_3Br_2S$ requires C, 47·3; H, 2·9%). Further bromination in chloroform slowly converted this dibromophenol into 3 : 5 : 4′-tribromo-4-hydroxydiphenyl (see above).

Action of Nitrous Acid on 3 : 5-*Dibromo*-4-*hydroxydiphenyl*.—Various amounts of sodium nitrite (1—2 mols.) and acetic acid were tried, and the following is a typical experiment. To a solution of the dibromophenol (10·9 g.) in acetic acid (100 c.c.), sodium nitrite (3·6 g.), dissolved in the minimum quantity of water, was added. After ¼ hour, the mixture was warmed on the steam-bath for a few minutes and then poured into water. The oily product obtained slowly solidified; after being dried, and fractionally crystallised from chloroform, it gave two pure products. The less soluble formed yellow, lustrous plates, m. p. 152° (Found: C, 55·7; H, 3·0%), identical with 3 : 5-dinitro-4-hydroxydiphenyl (Calc.: C, 55·4; H, 3·1%) prepared by the method of Garciá Banús and Guiteras (*loc. cit.*). The more soluble portion, which formed golden-yellow needles, m. p. 76°, was 5-*bromo*-3-*nitro*-4-*hydroxydiphenyl* (Found: C, 49·1; H, 3·1. $C_{12}H_8O_3NBr$ requires C, 49·0; H, 2·7%). Only gummy products were formed when 3 : 5-dibromo-4-hydroxydiphenyl was treated with nitric acid (1 mol.).

Action of Nitrous Acid on 3 : 5 : 4′-*Tribromo*-4-*hydroxydiphenyl*.—To this tribromophenol (2·2 g.) in hot acetic acid (33 c.c.) was added sodium nitrite (0·6 g.), and the solution was poured into water. The bulk of the product consisted of 5 : 4′-dibromo-3-nitro-4-hydroxydiphenyl (above).

Action of Nitric Acid on 3-*Bromo*-4-*hydroxydiphenyl*.—To this bromophenol (5·2 g.) in acetic acid (25 c.c.) was added nitric acid (1·5 c.c.) in acetic acid (10 c.c.). The reaction was completed by warming, the mixture poured into water, and the precipitated mass filtered off and fractionally crystallised from chloroform–light petroleum. It was thus separated into 3 : 5-dinitro-4-hydroxydiphenyl, 5-bromo-3-nitro-4-hydroxydiphenyl, and a small amount of 5-bromo-3 : 4′-dinitro-4-hydroxydiphenyl (see below).

3-Bromo-4′-nitro-4-hydroxydiphenyl.—To a suspension of 4′-nitro-4-hydroxydiphenyl (4 g.) in boiling chloroform (70 c.c.) was added bromine (3 g.) in chloroform (10 c.c.), and the resultant solution was evaporated. The residue crystallised from aqueous acetic acid as a pale yellow powder, m. p. 132° (Found : C, 49·6; H, 3·0. $C_{12}H_8O_3NBr$ requires C, 49·0; H, 2·7%).

5-Bromo-3 : 4′-dinitro-4-hydroxydiphenyl.—To 3-bromo-4′-nitro-4-hydroxydiphenyl (3 g.) in warm acetic acid (20 c.c.) was added nitric acid (0·8 c.c.) in acetic acid (5 c.c.). The liquid immediately filled with golden-yellow needles, which, after crystallisation from acetic acid, melted at 218° (Found : C, 42·1; H, 2·4. $C_{12}H_7O_5N_2Br$ requires C, 42·5; H, 2·1%).

In conclusion, the authors wish to express their thanks to Dr. J. Kenyon for his interest in this work, and to the Advisory Council of the Department of Scientific and Industrial Research for a grant made to one of them.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, March 1st, 1927.*]

CLVI.—*Higher Substitution Products of 4-Aminodiphenyl.*

By HAROLD ARCHIBALD SCARBOROUGH and WILLIAM ALEXANDER WATERS.

THE study of the substitution reactions of the monoacid bases of the diphenyl series (J., 1926, 557; this vol., p. 89) has been extended to include an examination of the products obtained by the further substitution of 3-chloro-4-aminodiphenyl, 3-nitro-4-aminodiphenyl, and their acetyl derivatives.

In every case, the introduction of one more substituent group into the free base proceeds with great ease at room temperature, and leads invariably to a product substituted in the 5-position. Thus 3-chloro- and 3-nitro-4-aminodiphenyl, on treatment with bromine in dilute acetic acid solution, yield 3-chloro-5-bromo-4-aminodiphenyl and 5-bromo-3-nitro-4-aminodiphenyl respectively. The introduction of any further substituent requires more drastic methods, particularly in the case of the 5-bromo-3-nitro-4-aminodiphenyl, and the substituent enters the 4′-position.

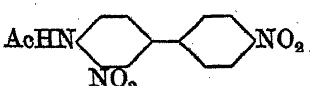
In contrast to the observed reactivity of the free bases, it is found that the further substitution of their acetyl derivatives proceeds only at high temperatures, in the presence of catalysts, or under other drastic conditions, and in every case the substituent enters the 4′-position. Thus 3-chloro-4-acetamidodiphenyl can be monobrominated by the use of pyridine as a catalyst, and mononitrated by dissolving it in nitric acid (*d* 1·4) at room temperature.

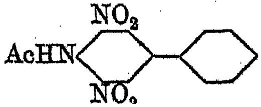
By still more drastic treatment, it has been found possible to obtain a dinitro-substitution product, which is probably 3-chloro-5 : 4′-dinitro-4-acetamidodiphenyl, but there is no evidence of the formation of a dibromo-derivative, although the free base, 3-chloro-4′-bromo-4-aminodiphenyl, can be brominated with great ease to yield 3-chloro-5 : 4′-dibromo-4-aminodiphenyl.

3-Nitro-4-acetamidodiphenyl is still less reactive, for it is only partly chlorinated by the prolonged action of dry chlorine in boiling glacial acetic acid solution, whilst bromination with the use of pyridine as a catalyst leads to only a 60% yield of 4′-bromo-3-nitro-4-aminodiphenyl, identical with the product obtained by Le Fèvre and Turner (J., 1926, 2045) by the nitration of 4′-bromo-4-acetamidodiphenyl.

The dinitration of 4-acetamidodiphenyl leads to a quantitative yield of 3 : 4′-dinitro-4-acetamidodiphenyl (I), for which the structure of 3 : 5-dinitro-4-acetamidodiphenyl (II) had previously been suggested by Fichter and Sulzberger (*Ber.*, 1904, **37**, 878) without any proof having been given.

(I.)





(II.)

The corrected structure (I) follows from the fact that the substance can be oxidised to *p*-nitrobenzoic acid.

From an examination of all recorded disubstitution reactions of 4-aminodiphenyl and its derivatives it may be seen that, whereas the free base yields derivatives substituted in the 3- and 5-positions, the acetyl derivative yields derivatives substituted in the 3- and 4′-positions.

This difference in mode of reaction must probably be ascribed to the inhibiting effect of the acetyl group, which decreases the activating power of the amino-group on the adjacent 3- and 5-positions in the same ring to such an extent that the normal ortho-para directive influence of the phenyl group predominates and leads to substitution in the 4′-position.

Although a substituted amino-group normally leads to substitution in the same ring in the first instance, thus showing that the difference in the type of the reaction cannot be solely due to steric hindrance, yet there are recorded instances in which substitution takes place initially in the 4′-position in the opposite ring. Of these, the bromination of 4-acetamidodiphenyl and the nitration of 2-acetamidodiphenyl have already been noted by the authors, and it has been suggested (J., 1926, 557) that these differences may possibly arise in consequence of differences of mechanisms of the substitution reactions. In particular, it has been thought possible that the initial rapid substitution in the same ring as an acetamido-group may be brought about by a mechanism involving an initial attack on the " side chain " followed by a migration reaction (which has been proved to yield the same type of product), and that the far slower substitution in the opposite ring might be due to a direct attack of the substituting group on the aromatic nucleus.

In an attempt to test this hypothesis, an examination of the reactivity towards substitution reagents of diacetyl-4-aminodiphenyl and of 4-phthalimidodiphenyl, which do not contain any hydrogen atom available for indirect attack, has been carried out. In each case it has been found that the reactivity of the molecule was still further decreased by the complete substitution of the amino-group, but unfortunately it has not been possible to isolate any definite substitution products.

4-Diacetylaminodiphenyl could not be attacked under conditions which did not first bring about hydrolysis of at least one of the acetyl groups, whilst 4-phthalimidodiphenyl was found to be too insoluble in the common reagents to be attacked except under conditions which lead to complete decomposition.

It may be noted, however, that the nitration of 4-benzylideneaminodiphenyl (Bell and Kenyon, J., 1926, 2707) and of 4-diphenylyltrimethylammonium nitrate (Vorländer, *Ber.*, 1925, **58**, 1893) in the 4′-position affords direct support for the view that substitution in the 4′-position is a direct reaction which will occur preferentially when indirect substitution is precluded.

As the disubstitution of 4-acetamidodiphenyl would seem to lead generally to substitution in the opposite ring, it would appear that the presence of a substituent group in the adjacent 3-position must also inhibit further substitution in the same ring. In accordance with the statement of Chattaway and Dowden (J., 1924, **125**, 1195) that the migration of a *N*-halogeno-derivative of a substituted acetanilide proceeds less and less readily as the number of substituent groups, especially nitro-groups, is increased, it may be suggested that the observed effect is due to the inhibition of any indirect reactions.

The effect of the nitro-group in 3-nitro-4-acetamidodiphenyl is most marked, for it would seem that not only does it prevent further substitution from taking place in the same ring, but also that it decreases the velocity of substitution in the other ring. This effect is in agreement with the known general effect of the nitro-group in making substitution more difficult to carry out, and it may be used to provide an explanation of the cases of unsymmetrical substitution in the diphenyl series which have been investigated recently.

For example, in the substitution of 4 : 4′-dichlorodiphenyl (compare Le Fèvre and Turner, J., 1926, 476, 2041) the C_6H_4Cl-group in the first instance has a stronger directive influence than the chlorine atom, and thus substitution occurs in the 2-position, but in the resultant compound the nitro-group has so reduced the directive power of the substituted phenyl group $C_6H_3(NO_2)Cl\cdot$ that the chlorine atom has the predominating directive influence, and in consequence a 3′-substituted derivative is produced.

The unsymmetrical nitration of diphthalylbenzidine may be explained similarly, and it may be noted that here also the phthalyl group plays the part of an inhibitor, in enabling the substituted phenyl group ($-C_6H_4\cdot N{:}Phth$) to have a more powerful directive influence than the substituted amino-group ($-N{:}Phth$) in the first instance (compare Brady, Quick, and Welling, J., 1925, **127**, 2265).

EXPERIMENTAL.

3-*Chloro-5-bromo-4-aminodiphenyl*.—3-Chloro-4-aminodiphenyl (J., 1926, 560), dissolved in cold glacial acetic acid, containing an excess of powdered anhydrous sodium acetate, was treated with bromine (1 mol.) as a 10% solution in the same solvent. The product was separated after 5 minutes by pouring the mixture into water; it crystallised from alcohol in colourless needles, m. p. 107° (Found: 0·1515 g. gave 0·1774 g. of silver halides. Calc. weight, 0·1776 g.). The *benzoyl* derivative crystallised from methyl alcohol in fine needles, m. p. 222° (Found: 0·1633 g. gave 0·1401 g. of silver halides. Calc. weight, 0·1400 g.).

3-*Chloro-5-bromodiphenyl*, obtained from the base by the elimination of the amino-group in the usual manner, formed pale yellow needles, m. p. 29°, b. p. 225°/30 mm. (Found: 0·2283 g. gave 0·2846 g. of silver halides. Calc. weight, 0·2827 g.). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded 3-chloro-5-bromobenzoic acid (m. p. 193°).

3-*Chloro-5 : 4′-dibromo-4-aminodiphenyl*.—3-Chloro-5-bromo-4-aminodiphenyl was boiled for 3 hours with an excess of bromine in glacial acetic acid solution. The solid which was separated by pouring the mixture into water proved to be partly acetylated, and therefore was hydrolysed by boiling it for 6 hours with alcoholic hydrochloric acid. The pure base then separated, and crystallised from alcohol in long needles, m. p. 129° (Found: 0·2010 g. gave 0·2885 g. of silver halides. Calc. weight, 0·2888 g.). By boiling this base for 8 hours with acetic acid and acetic anhydride, the *diacetyl* derivative was obtained, crystallising from dilute acetic acid in white needles, m. p. 147° (Found: C, 42·9; H, 2·8. Calc.: C, 43·05; H, 2·7%. 0·1716 G. gave 0·2007 g. of silver halides. Calc. weight, 0·2013 g.).

3-*Chloro*-4′-*bromo*-4-*acetamidodiphenyl*.—5 G. of 3-chloro-4-acetamidodiphenyl (*loc. cit.*), 10 g. of anhydrous sodium acetate, and 1 c.c. of pyridine were intimately mixed together, 5 c.c. of bromine were added slowly, and the mixture was heated at 100° for 3 hours. The product was separated from the reaction mixture in 60% yield by repeated crystallisation from methyl alcohol and from dilute acetic acid, and formed white needles, m. p. 185° (Found: 0·1600 g. gave 0·1630 g. of silver halides. Calc. weight, 0·1633 g.). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded *p*-bromobenzoic acid (m. p. 252°). The corresponding *base*, obtained by boiling the acetyl derivative for 4 days with 20% alcoholic hydrochloric acid, crystallised from methyl alcohol in white needles, m. p. 108° (Found: 0·1208 g. gave 0·1421 g. of silver halides. Calc. weight, 0·1417 g.). The base on warming with bromine in acetic acid yielded 3-chloro-5 : 4′-dibromo-4-aminodiphenyl which, alone or mixed with the product obtained by the alternative method, melted at 129°.

3-*Chloro*-4′-*nitro*-4-*acetamidodiphenyl*.—3-Chloro-4-acetamidodiphenyl was gradually dissolved in nitric acid (*d* 1·4) at room temperature, and after ½ hour the solution was poured on ice. The solid produced was washed with dilute ammonia and dissolved in a large volume of alcohol, from which it was deposited, on cooling, in fine yellow needles, m. p. 220·5° (Found: N, 9·4; Cl, 12·1. $C_{14}H_{11}O_3N_2Cl$ requires N, 9·6; Cl, 12·2%). On oxidation with chromic anhydride in glacial acetic acid solution, *p*-nitrobenzoic acid (m. p. 240°) was produced.

3-*Chloro*-5:4′-*dinitro*-4-*acetamidodiphenyl*.—3-Chloro-4-acetamidodiphenyl was gradually dissolved in nitric acid (*d* 1·5) at room temperature, and after 3 hours the solution was poured on ice. The solid produced was washed with dilute ammonia and extracted with alcohol; the residue crystallised from a large volume of methyl alcohol in fine, pale yellow needles, m. p. 250° (Found: N, 12·7; Cl, 10·55. $C_{14}H_{10}O_5N_3Cl$ requires N, 12·5; Cl, 10·55%). The substance was not oxidised by boiling with chromic anhydride in glacial acetic acid solution. Such stability is characteristic of diphenyl derivatives containing a nitro-group in each ring.

5-*Bromo*-3-*nitro*-4-*aminodiphenyl.*—3-Nitro-4-aminodiphenyl (Fichter and Sulzberger, *loc. cit.*), dissolved in glacial acetic acid at 30–40°, was treated gradually with bromine (1 mol.) as a 10% solution in the same solvent. The product was separated after ½ hour by pouring the mixture into water, and, on attempted crystallisation from any of the common solvents, formed a very flocculent, orange-yellow mass of m. p. 99—101° which could not be freed from traces of more highly brominated substances (Found: Br, 30·1, 29·95. $C_{12}H_9O_2N_2Br$ requires Br, 27·3%). A similar mixture was obtained by the bromination of 3-nitro-4-aminodiphenyl in chloroform solution. An attempt at separation of a pure product by acetylation of the mixture was not successful.

By eliminating the amino-group in the usual manner, *5-bromo-3-nitrodiphenyl* was obtained in a pure form in more than 60% yield. It crystallised from alcohol in pale yellow needles, m. p. 72°, b. p. 240—250°/30 mm. (Found: Br, 28·8. $C_{12}H_8O_2NBr$ requires Br, 28·8%). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded 5-bromo-3-nitrobenzoic acid (m. p. 159—160°).

5 : 4′-*Dibromo*-3-*nitro*-4-*aminodiphenyl.*—5-Bromo-3-nitro-4-aminodiphenyl was heated at 100° for 6 hours with excess of bromine in glacial acetic acid solution, and the product, which was separated by pouring the mixture into water, was recrystallised from dilute acetic acid, forming red needles, m. p. 158° (Found: Br, 42·9. $C_{12}H_8O_2N_2Br_2$ requires Br, 43·0%). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded *p*-bromobenzoic acid (m. p. 253°).

The same product was obtained in poor yield by boiling 3-nitro-4-acetamidodiphenyl for 4 days with a large excess of bromine in glacial acetic acid solution.

4′-*Chloro*-3-*nitro*-4-*acetamidodiphenyl.*—Chlorine was passed for 4 hours into a solution of 10 g. of 3-nitro-4-acetamidodiphenyl and 20 g. of anhydrous sodium acetate in 200 c.c. of boiling glacial acetic acid. After cooling, excess of chlorine was removed with a current of air and water was added; a red gum was then deposited. This was extracted with hot alcohol and yielded 3 g. of bright yellow needles, m. p. 199° (Found: Cl, 12·15. $C_{14}H_{11}O_3N_2Cl$ requires Cl, 12·2%). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded *p*-chlorobenzoic acid (m. p. 240°).

The corresponding *base* was obtained by boiling the acetyl derivative for 4 hours with 20% alcoholic hydrochloric acid, and crystallised from dilute acetone in scarlet needles, m. p. 174° (Found: Cl, 14·4. $C_{12}H_9O_2N_2Cl$ requires Cl, 14·3%).

4′-*Bromo*-3-*nitro*-4-*acetamidodiphenyl*.—5 G. of 3-nitro-4-acetamidodiphenyl, 10 g. of powdered anhydrous sodium acetate, and 1 c.c. of pyridine were intimately mixed together, 5 c.c. of bromine were gradually added, and the mixture was heated at 100° for 8 hours. The brominated product was isolated from the reaction mixture in 60% yield by extraction with acetone, and crystallised from that solvent in fine yellow plates, m. p. 207—208° (Found: Br, 24·0. Calc. for $C_{14}H_{11}O_3N_2Br$: Br, 23·9%). On oxidation with chromic anhydride in glacial acetic acid solution it yielded *p*-bromobenzoic acid (m. p. 253°). On hydrolysis with 20% alcoholic hydrobromic acid, the corresponding base was obtained, crystallising readily from dilute acetone in scarlet needles, m. p. 175° (Found: Br, 27·3. Calc. for $C_{12}H_9O_2N_2Br$: Br, 27·3%). Both the acetyl derivative and the base are obviously identical with the products obtained by Le Fèvre and Turner (J., 1926, 2045) by the nitration of 4′-bromo-4-acetamidodiphenyl.

3 : 4′-*Dinitro*-4-*acetamidodiphenyl*.—10 G. of 3-nitro-4-acetamidodiphenyl, dissolved in a mixture of 20 c.c. of concentrated sulphuric acid and 10 c.c. of glacial acetic acid at 0°, were treated during 2 hours with a mixture of 6 c.c. of fuming nitric acid and 14 c.c. of glacial acetic acid. After 24 hours, the product was poured on ice, and the yellow solid produced crystallised from glacial acetic acid and then from a large volume of acetone. From the latter solvent it formed long, pale yellow needles, m. p. 243—244° (corr.), obviously identical with the dinitro-4-acetamidodiphenyl, m. p. 240—241° (uncorr.), of Fichter and Sulzberger (*loc. cit.*). The same substance could be obtained more easily by dissolving 4-acetamidodiphenyl in cold fuming nitric acid and pouring the solution on ice after 30 minutes.

On prolonged oxidation with chromic anhydride in glacial acetic acid solution, *p*-nitrobenzoic acid (m. p. 240—241°) was produced, showing conclusively that the second nitro-group had entered the 4′- and not the 5-position.

The corresponding *base* was obtained by boiling 5 g. of the acetyl derivative with a mixture of 10 c.c. of concentrated sulphuric acid and 200 c.c. of alcohol for 2 days. It crystallised from a large bulk of alcohol in orange plates, m. p. 233—234°, corresponding exactly in properties with the base of Fichter and Sulzberger.

3 : 4′-*Dinitrodiphenyl*, obtained from the base by the elimination of the amino-group in the usual manner, crystallised from acetone in pale yellow needles, m. p. 189° (Found: N, 11·5. Calc.: N, 11·5%). Mention has already been made of the use of this compound for structure determination (this vol., p. 96).

Diacetyl-4-*aminodiphenyl* was obtained by boiling 4-acetamidodiphenyl (10 g.) with acetic anhydride (50 c.c.) and anhydrous sodium acetate (5 g.) for 6 hours. It crystallised from light petroleum (b. p. 60—80°) in fine, white needles, m. p. 121° (Found: C, 75·55; H, 6·0. $C_{16}H_{15}O_2N$ requires C, 75·85; H, 5·9%).

It was not attacked by chlorine in cold 5% solution, but was hydrolysed on warming in presence of chlorine. There was no action on warming with 1 mol. of bromine in presence of anhydrous sodium acetate and a drop of pyridine, but complete decomposition occurred when a large excess of bromine was used.

On dissolving the diacetyl compound in nitric acid (*d* 1·4) at 0° and pouring the solution into ice and water after 10 minutes, a nitrated mixture was formed from which were separated pure specimens of 3-nitro-4-(mono)acetamidodiphenyl, m. p. 132°, and 3 : 4′-dinitro-4-(mono)acetamidodiphenyl, m. p. 244°; both were identified by mixed melting-point determinations with specimens obtained by the normal methods, and occurred in such quantities as to correspond to more than 70% of the theoretical yield of nitrated products.

4-*Phthalimidodiphenyl* was prepared by heating equivalent quantities of phthalic anhydride and 4-aminodiphenyl at 160° for 6 hours. It was a white powder, m. p. 288°, almost insoluble in all low-boiling solvents, but could be purified by long-continued extraction, in a Soxhlet apparatus, with boiling benzene. For analysis, it was separated twice from a large bulk of toluene and finally from xylene (Found: C, 80·3; H, 4·3. $C_{20}H_{13}O_2N$ requires C, 80·25; H, 4·4%).

The substance was insoluble in fuming nitric acid at room temperature, and was not attacked by bromine in presence of pyridine at 100°. It was decomposed completely by nitration in a large volume of concentrated sulphuric acid.

All the m. p.'s recorded in this paper have been corrected, and where necessary the identity of a substituted benzoic acid has been established by the "mixed m. p." method.

The authors beg to thank the Chemical Society for a grant from the Research Fund. One of them (W. A. W.) is indebted to the Master and Fellows of Gonville and Caius College for a studentship which has enabled him to collaborate in this work.

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[*Received, March 5th*, 1927.]

CLVII.—*The Iodination of* o-*Nitrophenol.*

By HERBERT HENRY HODGSON.

HÜBNER (*Ber.*, 1874, 7, 461) described, but did not analyse, two iodonitrophenols, termed by him α and β, m. p. 90—91° and 66—67°, respectively, which he obtained by iodinating *o*-nitrophenol in glacial acetic acid in presence of mercuric oxide, and separated by fractionally crystallising their potassium salts from alcohol. The α-compound is stated to be only slowly volatile in steam, the β much more readily, and both were assumed to be monoiodonitrophenols.

In Beilstein's " Organische Chemie " (II, p. 700), the α- and the β-compound are recorded as 5(?)-iodo-2-nitrophenol and 6(?)-iodo-2-nitrophenol, respectively. Roberts (J., 1923, **123**, 2708) doubts whether they are pure substances, since neither is identical with his 4-iodo-2-nitrophenol (m. p. 80—81°) or with Brenans's 2-iodo-6-nitrophenol (m. p. 110°) or2-iodo-4-nitro phenol (m. p. 86—87°) (*Compt. rend.*, 1902, **134**, 357). Keimatsu (*J. Pharm. Soc. Japan*, 1924, No. 507, 319) regards the Hübner compounds as 3- and 4-iodo-2-nitrophenols. If this is so, the former would be an example of an unexpected type of iodination.

The present author, having already prepared 5-iodo-2-nitrophenol (m. p. 96°) and 3-iodo-2-nitrophenol (m. p. 73·5°) (this vol., p. 630) is in possession of the necessary standards for the solution of this problem. He has found that in all cases of direct iodination of *o*-nitrophenol with the aid of mercuric oxide, whether the quantity of iodine taken is less than, equal to, or greater than that required for mono-iodination according to the equation $2NO_2\cdot C_6H_4\cdot OH + 2I_2 + HgO = 2NO_2\cdot C_6H_3I\cdot OH + HgI_2 + H_2O$, di-iodination occurs to a considerable extent and various quantities of mercurous salts are also produced. Hübner's α- and β-compounds have proved to be 4 : 6-di-iodo-2-nitrophenol and 4-iodo-2-nitrophenol, respectively, mixed with small quantities of 6-iodo-2-nitrophenol. The mono-iodo-2-nitrophenols are all readily volatile in steam.

The considerable tendency toward di-iodination, and the formation of 4-iodo-2-nitrophenol in excess of that of the 6-iodo-isomeride, indicate that the initial mono-iodination of *o*-nitrophenol occurs preferentially in position 4. No indication of the presence of 3-iodo-2-nitrophenol has been detected.

EXPERIMENTAL.

For purposes of comparison, 6-iodo-2-nitrophenol (m. p. 110°) and 4-iodo-2-nitrophenol (m. p. 80—81°) were prepared by direct nitration of 2- and 4-iodophenols, respectively; 4 : 6-di-iodo-2-nitrophenol (m. p. 98°) by direct iodination of *o*-nitrophenol in glacial acetic acid in presence of yellow mercuric oxide, by iodination of 4-iodo- and 6-iodo-2-nitrophenols, and by Roberts's method (*loc. cit.*); 6-iodo-2 : 4-dinitrophenol (m. p. 106°) and 4-iodo-2 : 6-dinitrophenol (m. p. 113°) by direct iodination of 2 : 4- and 2 : 6-dinitrophenols, respectively, and also by the dinitration of 2- and 4-iodophenols by Hodgson and Moore's method for the dinitration of *m*-chlorophenol (J., 1925, **127**, 1601).

Iodination by Hübner's Method.—A solution of *o*-nitrophenol (2 mols.) and iodine (2 mols.) in glacial acetic acid, while being vigorously shaken, was treated gradually with yellow mercuric oxide until the iodine had disappeared. The mixture was then filtered, and the filtrate diluted with water to precipitate the iodonitrophenols. These were washed by decantation, and treated with warm aqueous potassium hydroxide, and the filtered solution was evaporated to dryness. The solid residue was boiled with alcohol several times, and the combined extracts were allowed to cool; long, red needles were deposited, which were continually removed (α) until more tabular and yellower crystals began to appear (β). The two batches, α and β, were each treated with sulphuric acid, and then steam-distilled until the more volatile products had passed over. In each case, the slowly volatile material was crystallised several times from dilute alcohol, the melting point being thus raised from 94° to 98° (Found: I, 65·1. Calc. for $C_6H_3O_3NI_2$: I, 64·9%). Mixed with authentic 4 : 6-di-iodo-2-nitrophenol, the substances again melted at 98°. The potassium salts of these two compounds were alike in every way and different from the potassium salt of any of the monoiodo-2-nitrophenols.

The steam-volatile product in each case was recrystallised from alcohol until the m. p. had been raised from about 63° to 78° (Found for the compounds from the α- and the β-batch, respectively: I, 48·2, 48·1. Calc. for $C_6H_4O_3NI$: I, 47·9%). Mixed with authentic 4-iodo-2-nitrophenol, each compound melted at 79—80°, and the identity was further established (*a*) by iodination to 4 : 6-di-iodo-2-nitrophenol, (*b*) by nitration to 4-iodo-2 : 6-dinitrophenol, and (*c*) by nitration to picric acid without 3-iodo-2 : 4 : 6-trinitrophenol being detected.

The residual potassium salt from the original alcoholic extract (above) was suspended in dilute sulphuric acid and submitted to steam-distillation. The volatile product, after several crystallisations from alcohol, melted at 102° (Found: I, 48·0. Calc. for $C_6H_4O_3NI$: I, 47·9%). Its identity with 6-iodo-2-nitrophenol was indicated by the like crystalline forms, and by the melting point of a mixture of the two substances, and was confirmed (*a*) by iodination to 4 : 6-di-iodo-2-nitrophenol, (*b*) by nitration to 6-iodo-2 : 4-dinitrophenol, and (*c*) by trinitration to picric acid without 3-iodo-2 : 4 : 6-trinitrophenol being detected.

A slightly volatile product obtained in the above steam-distillation was 4 : 6-di-iodo-2-nitrophenol.

The same results were obtained when the iodination of *o*-nitrophenol was carried out at 40—50° ; when iodine, dissolved in ether, was added in small portions at a time, and the mixture was shaken during the gradual addition of mercuric oxide until the iodine had disappeared; and when alcohol was employed instead of glacial acetic acid as solvent.

Modifications of Hübner's Method.—(*a*) Instead of the potassium salts being prepared, the water-precipitated iodonitrophenols were steam-distilled, and several fractions collected. The earlier ones contained a little 6-iodo-2-nitrophenol, but consisted mainly of 4-iodo-2-nitrophenol. The later fractions contained a little 4 : 6-di-iodo-2-nitrophenol, and the residue was a mixture of this compound with mercurous and mercuric salts.

(*b*) The iodination was carried out as described above (*a*), but half the quantity of iodine was used. The steam-distillate was collected in three fractions, which were filtered off and extracted with boiling alcohol. The extract of the first fraction left a residue containing mercurous iodide, and deposited, on cautious dilution, crystals of 6-iodo-2-nitrophenol followed by an oil. The latter was dissolved in aqueous sodium hydroxide, the alcohol removed, and the solution was acidified and very slowly steam-distilled. The first-runnings deposited *o*-nitrophenol on cooling. The second fraction was treated similarly and found to contain mercurous iodide and 4- and 6-iodo-2-nitrophenols. The third fraction contained these substances and also 4 : 6-di-iodo-2-nitrophenol.

The original residue consisted mainly of 4 : 6-di-iodo-2-nitrophenol mixed with mercuric iodide.

(*c*) In this experiment, twice the quantity of iodine was used. The steam-volatile product was only small in amount, had a high m. p., and contained mercury. The bulk of the reaction product was the very slightly volatile 4 : 6-di-iodo-2-nitrophenol.

Evidence of the Absence of 3-*Iodo*-2-*nitrophenol.*—The entire water-precipitated mixture of iodonitrophenols obtained in an experiment according to Hübner was washed, dried, and divided into three equal portions. One of these was mixed with *m*-iodophenol, another with 3-iodo-2-nitrophenol, and the two mixtures and the third portion were separately trinitrated, and the products were worked up, by the methods used in the trinitration of *m*-iodophenol (*loc. cit.*, p. 634). The mixture containing *m*-iodophenol and that containing 3-iodo-2-nitrophenol each gave a sublimate of 3-iodo-2 : 4 : 6-trinitrophenol, but the third portion of the Hübner product gave only picric acid. This result indicates the absence of 3-iodo-2-nitrophenol from this product.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 7th*, 1927.]

CLVIII.—*The Action of Caustic Alkalis on the 3-Halogeno-4-nitrosodimethylanilines.*

By HERBERT HENRY HODGSON and JOHN SAMUEL WIGNALL.

IN view of the conversion of 4-nitroso-3-chloro- and -3-bromo-phenols into their tautomerides, the 3-chloro- and 3-bromo-benzoquinone-4-oximes (Hodgson and Moore, J., 1923, **123**, 2499; 1925, **127**, 2260), it appeared desirable to ascertain whether the latter substances could be produced directly by the action of alkali hydroxide on the 3-halogeno-4-nitrosodimethylanilines. This result was obtained with the 3-chloro- and the 3-bromo-compound, but 3-iodo-4-nitrosodimethylaniline lost iodine when boiled with aqueous alkali hydroxide.

3-*Iododimethylaniline* and its 4-*nitroso*-derivative do not appear to have been prepared before. An improved method is described for making the 3-halogenodimethylanilines. The purity of preparations of 3-bromo-4-nitrosodimethylaniline described in the literature has hitherto been in doubt.

EXPERIMENTAL.

Preparation of the 3-Halogenodimethylanilines.—The 3-halogenoaniline (1/20 g.-mol.), methyl alcohol (12 c.c.), and methyl sulphate (15 c.c.) are mixed together, heat being evolved. When this has abated, the mixture is heated for 6 hours in a sealed tube. Dimethylation of 3-chloro- and of 3-bromo-aniline occurs at 165°, but 3-iodoaniline requires a temperature of 175° (it chars at 185°). The product is poured into water and made faintly alkaline, and the oil thus liberated is quickly separated, since otherwise emulsification readily takes place. The oil is washed, dried with calcium chloride, and distilled.

The bulk of the 3-chlorodimethylaniline distils between 230° and 233° and has b. p. 231° (Stadel, *Ber.*, 1883, **16**, 32, and Joubert, *Bull. Soc. chim.*, 1874, **21**, 24, give b. p. 231°) (Found: Cl, 22·7. Calc.: Cl, 22·8%).

3-Bromodimethylaniline distils between 244—245° and at 175°/

120 mm., and has b. p. 245° (Wurster, *Ber.*, 1879, **12**, 1818, gives b. p. 259°) (Found: Br, 40·1. Calc.: Br, 40%).

3-*Iododimethylaniline* has b. p. 215—216°/190 mm., but decomposes when distilled under atmospheric pressure (Found: I, 51·6. $C_8H_{10}NI$ requires I, 51·4%).

The 3-halogenodimethylanilines are viscous liquids which dissolve slowly in dilute mineral acids, but readily in the concentrated acids and then remain in solution on dilution.

Preparation of the 3-*Halogeno*-4-*nitrosodimethylanilines*.—A solution of the 3-halogenodimethylaniline (1/20 g.-mol.) in concentrated hydrochloric acid (16 c.c.) is diluted with water (60 c.c.), cooled to 0°, and treated slowly with sodium nitrite (7 g. in 35 c.c. of water). After an hour's stirring the yellow hydrochloride of the 3-halogeno-4-nitrosodimethylaniline is collected, and the green base is liberated from it and crystallised from methyl alcohol. The three compounds all crystallise in dark green needles.

3-Chloro-4-nitrosodimethylaniline has m. p. 130° (decomp.) (Stadel and Joubert, *locc. cit.*, do not record the m. p.) (Found: Cl, 19·1. Calc.: Cl, 19·2%).

3-Bromo-4-nitrosodimethylaniline has m. p. 129° (decomp.). Wurster (*loc. cit.*) gives m. p. 145°, Vorländer and Siebert (*Ber.*, 1919, **52**, 283) give m. p. 116°, and Kharasch and Piccard (*J. Amer. Chem. Soc.*, 1920, **42**, 1855) give m. p. 148°. The purifying process employed by Kharasch and Piccard is unnecessary when the 3-bromodimethylaniline used has been prepared by the method described above, nitrosation then proceeding smoothly. The above product, m. p. 129°, after treatment according to Kharasch and Piccard, remained unchanged; it still melted at 129°, and did not give the Liebermann nitroso-reaction—the test of purity employed by those authors (Found: Br, 34·7. Calc.: Br, 34·9%). The presence of under-methylated or of unchanged amine appreciably interferes with the nitrosation, and the product then obtained resinifies when kept.

3-*Iodo*-4-*nitrosodimethylaniline* has m. p. 128° (decomp.) (Found: I, 46·1. $C_8H_9ON_2I$ requires I, 46·0%). Like the corresponding chloro- and bromo-analogues, it is soluble with difficulty in methyl or ethyl alcohol, benzene, toluene, or ether, and insoluble in light petroleum or carbon tetrachloride.

Action of Aqueous Alkalis on the 3-*Halogeno*-4-*nitrosodimethylanilines*.—3-Chloro- or 3-bromo-4-nitrosodimethylaniline is boiled with a large excess of 10% halogen-free aqueous sodium or potassium hydroxide until almost complete solution is attained, dimethylamine being expelled. The filtered solution, when rendered just acid in the cold, gives a precipitate of the almost colourless form of 3-chloro-

or 3-bromo-benzoquinone-4-oxime, m. p. 175° and 190°, respectively (Found: Cl, 22·4. Calc.: Cl, 22·5%. Found: Br, 39·6. Calc.: Br, 39·6%). Comparison of the products, recrystallised from benzene (m. p. 178° and 190°, respectively), with Hodgson and Moore's (*loc. cit.*) preparations made by direct nitrosation of 3-chloro- and 3-bromo-phenol, and subsequent conversion by means of alkalis, established identity.

3-Iodo-4-nitrosodimethylaniline is decomposed by the above treatment into compounds of indefinite character with elimination of iodine. No similar removal of halogen occurs with the 3-chloro- and the 3-bromo-compound.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 19th, 1927.*]

CLIX.—*Acid and Salt Effects in Catalysed Reactions. Part VIII. The Determination of Hydrolytic Velocity Coefficients from Isocatalytic Data. Reaction Velocities in Buffer Solutions and Compound Catalytic Catenaries.*

By HARRY MEDFORTH DAWSON.

IN accordance with the theory outlined in previous papers (see, *e.g.*, this vol., p. 461), the velocity of hydrolytic reactions * has a minimum value when the hydrogen-ion concentration is that given by the equation

$$[H^+]_i = \sqrt{k_{OH}K_w/k_h} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At this point the partial velocities due respectively to the hydrogen ion and the hydroxyl ion are equal, and the total ionic reaction velocity is given by

$$u_i = 2\sqrt{k_h k_{OH} K_w} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From these equations, the isocatalytic data $[H^+]_i$ and u_i can be calculated if the coefficients k_h and k_{OH} are known; or, alternatively, the derived equations

$$2k_h = u_i/[H^+]_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2k_{OH} = u_i[H^+]_i/K_w \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$k_{OH}/k_h = [H^+]_i^2/K_w \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

enable the converse calculations to be made. It is apparent that the derivation of k_{OH} or k_{OH}/k_h involves a knowledge of the ionisation product of the solvent, but that this is not required for the determination of k_h.

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* The term hydrolytic reaction is used in this paper for any reaction which is catalysed by both the hydrogen and the hydroxyl ion.

The consideration of hydrolytic reactions from the point of view of the experimental measurement of the four quantities k_h, k_{OH}, $[H^+]_i$ and u_i is a matter of some interest. For those reactions in which undissociated water molecules take no measurable part, the ionic reaction velocity u may be identified with the actually measured velocity (v) and it is with reactions of this type that the present paper is primarily concerned. The procedure followed in the determination of k_h and k_{OH} is well known, and it need only be mentioned that attempts to measure v_i and $[H^+]_i$ have been made for the most part by the use of buffer solutions of varying p_H value.

In general, it is not possible to determine each of the four quantities k_h, k_{OH}, v_i, and $[H^+]_i$ by direct measurement, but the hydrolysis of aliphatic esters affords instances in which this may be readily accomplished, so far as the time factor is concerned. When the velocities of reaction, as measured by k_h and k_{OH}, are very much smaller, the direct measurement of v_i and $[H^+]_i$ may be attended with difficulties, as, for instance, in the case of the hydrolysis of aromatic amides at the ordinary temperature.

For some reactions, the relations may be such that only one of the velocity coefficients can be measured in the ordinary way. If, for instance, the ratio k_{OH}/k_h is of the order of 10^5, it is obvious that only one of the coefficients can be obtained directly from experiment. Quite apart from the difference in the order of magnitude of the coefficients, the transition from acid to alkaline solution may be complicated by the incidence of other reactions, concurrent or consecutive, which interfere with the measurement of the reaction velocity in question. Such complications occur in the acetone–iodine reaction, for which the value of k_h can be determined quite conveniently, but since the ratio k_{OH}/k_h is about 40,000, it is apparent that the direct measurement of k_{OH} would not be a simple matter even under the most favourable conditions. In actual fact, the measurement is precluded by the circumstance that subsequent reactions, leading to the production of iodoform, effectively mask the relations which characterise the primary stage of the acetone–iodine reaction in solutions of $p_H > 6$. In this particular instance, however, it has been found possible to determine the value of $[H^+]_i$ from observations on the velocity of the autocatalysed reaction (Dawson and Powis, J., 1912, **101**, 1503; Dawson, this vol., p. 458), and by combining this with k_h, the values of v_i and k_{OH} may be derived from equations (3) and (4).

Other hydrolytic reactions are distinguished by the circumstance that the values of k_h and k_{OH} are both so large that neither can be determined directly. It is not improbable that many of the reactions associated with the phenomena of tautomerism, pseudo-acidity, etc., afford examples which belong to this group. In such cases, it may sometimes be possible to obtain the velocity coefficients from the measurements of v_i and $[H^+]_i$.

Reactions in Buffer Solutions.

Since the use of buffer solutions serves to provide the stabilised p_H conditions which are necessary for the determination of v_i and $[H^+]_i$ in the case of hydrolytic reactions, it is necessary to examine critically the factors which are involved in the employment of such solutions for this purpose. In the light of the results which have been described previously (Dawson and Carter, J., 1926, 2282), it cannot be assumed that the catalytic effect of the acid and salt in the buffer solution is negligible. If, for instance, the solution used is an acetate buffer of p_H 5, in which the total acetate concentration is $0{\cdot}02M$, the concentrations of the constituents for which catalytic activity has been demonstrated are $[H^+] = 10^{-5}$, $[OH^-] = 10^{-9}$, $[HA] = 6 \times 10^{-3}$, and $[A^-] = 14 \times 10^{-3}$. In other words, the concentrations of the acetic acid and of the acetate ion are, respectively, 6×10^6 and 14×10^6 times that of the hydroxyl ion. In such circumstances, the possible catalytic action of buffer constituents, other than the hydrogen and hydroxyl ions, cannot be ignored. It may, in fact, be shown that the use of buffer mixtures does not in general yield the isocatalytic data which are characteristic of the H^+–OH^- catenary.

For the sake of simplicity it will be assumed that the buffer mixture consists of a weak acid HA and its corresponding salt, and that the variation of p_H is brought about by altering the concentration of the salt whilst the concentration of the acid (c) is kept constant. If the acid is not too weak, and its concentration not too small, the use of such a series of buffer solutions would give a point of minimum velocity characterised by values of $[H^+]_i$ and v_i given by the equations

$$[H^+]_i = \sqrt{k_a K c/(k_h - k_m)} \quad . \quad . \quad . \quad . \quad (6)$$

and

$$v_i = 2\sqrt{(k_h - k_m) k_a K c} + k_m c \quad . \quad . \quad (7)$$

On the other hand, the isocatalytic data corresponding with the joint action of the hydrogen and hydroxyl ions are given by equations (1) and (2). In general, there will be a considerable difference between the two pairs of isocatalytic data. For the weaker acids which are commonly used in the preparation of buffer mixtures, k_m can be neglected in comparison with k_h and the difference between the two hydrogen-ion concentrations is essentially determined by the value of the ratio $k_a K c/k_{OH} K_w$. The difference would seem to disappear when $c = k_{OH} K_w/k_a K$. If the concentration of the acid has this value, the *M.V.* point actually realised does not correspond, however, with equations (1) and (2), *i.e.*, with the H^+–OH^- catenary, but minimum velocity is attained at a greater hydrogen-ion concentration, which indeed is characteristic of a catenary curve for which the anionic catalytic effect is shared by the acid ions A^- and OH^-. This catenary may conveniently be described as a compound catenary.

The Compound Catenary.—Under conditions in which the total catalytic effect of the negative ions is shared by A^- and OH^-, the equation for the velocity of reaction may be written

$$v = k_h[H^+] + k_a[A^-] + k_{OH}[OH^-] + k_m[HA] + k_w[H_2O] \quad . \quad (8)$$

Since $[A^-] = K(c-[H^+])/[H^+]$ and $[OH^-] = K_w/[H^+]$, equation (8) may be put in the form

$$v = (k_h - k_m)[H^+] + (k_aKc + k_{OH}K_w)/[H^+] + k_mc + k_wc_w - k_aK \quad (9)$$

and if the concentration (c) of the acid HA is constant, it is evident that the reaction velocity passes through a minimum when

$$[H^+] = [H^+]_i = \sqrt{(k_aKc + k_{OH}K_w)/(k_h - k_m)} \quad . \quad (10)$$

and by substitution in (9) the minimum velocity is given by

$$v_i = 2\sqrt{(k_h - k_m)(k_aKc + k_{OH}K_w)} + k_mc + k_wc_w \quad (11)$$

if the negligibly small term k_aK be left out of account. The relations involved are of exactly the same kind as those which have been already described in connexion with the catalytic activity of acid–salt mixtures of the type cHA + xMA, and it is obvious that the total catalytic effects are such that the reaction velocity, in its dependence on p_H, can be represented by a catenary curve symmetrical with reference to the point defined by equations (10) and (11).

These compound catenaries form a continuous series limited on the one side by the H^+–OH^- catenary, and on the other by the simple catenaries which correspond with the acid–salt mixtures of the type cHA + xMA, for which the effect of the hydroxyl ion can be ignored. The relation between the hydrogen-ion concentrations $[H^+]_i'$ characteristic of the *M.V.* points on the compound catenaries and the hydrogen-ion concentration $[H^+]_i$ of the *M.V.* point on the H^+–OH^- catenary is given by

$$[H^+]_i'/[H^+]_i = \sqrt{(k_aKc + k_{OH}K_w)/k_{OH}K_w}$$

or

$$(p_H)_i - (p_H)_i' = \tfrac{1}{2}\log m \quad . \quad . \quad . \quad . \quad (12)$$

where $m = (k_aKc + k_{OH}K_w)/k_{OH}K_w$.

The numerical relations involved may be illustrated by reference to the acetone–iodine reaction for which the requisite data are available. At 25° and an acetone concentration of 20 c.c. per litre, $k_{\mathrm{OH}}K_w = 2{\cdot}0 \times 10^{-13}$, and for acetic acid $k_aKc = 832 \times 10^{-13}c$. In Table I are shown the values of c, $k_aKc \times 10^{13}$, $\sqrt{m}$, and $(p_{\mathrm{H}})_i - (p_{\mathrm{H}})_i'$.

TABLE I.

c	0	0·0001	0·0002	0·0005	0·001
$k_aKc \times 10^{13}$	0	0·08	0·16	0·42	0·83
$\sqrt{m}$	1·0	1·02	1·04	1·10	1·19
$(p_{\mathrm{H}})_i - (p_{\mathrm{H}})_i'$	0	0·01	0·02	0·04	0·08
c	0·002	0·005	0·01	0·02	0·05
$k_aKc \times 10^{13}$	1·66	4·15	8·3	16·1	41·6
$\sqrt{m}$	1·35	1·75	2·27	3·05	4·67
$(p_{\mathrm{H}})_i - (p_{\mathrm{H}})_i'$	0·13	0·24	0·36	0·48	0·67

When the concentration of the acetic acid reaches 0·05*N*, the catalytic effect of the hydroxyl ion can be almost neglected and the end of the series of compound catenaries may be said to have been reached. The non-interference of the $\mathrm{H^+}$–$\mathrm{A^-}$ and $\mathrm{H^+}$–$\mathrm{OH^-}$ catenaries may therefore be said to require that the difference in the p_{H} values of the *M.V.* points should not be less than about 0·7 p_{H} unit.

The gradual displacement of the *M.V.* point in passing from the $\mathrm{H^+}$–$\mathrm{OH^-}$ catenary to the simple $\mathrm{H^+}$–$\mathrm{A^-}$ catenaries is possibly best illustrated by reference to the exponential curves which represent the catalytic effect of the hydrogen ion on the one hand and the combined catalytic effect of the anions on the other. In adopting this method of comparing the relations, it is assumed that the acid HA is weak and that the coefficient k_m can be neglected in comparison with k_h. In these circumstances, the partial ionic reaction velocities are given by

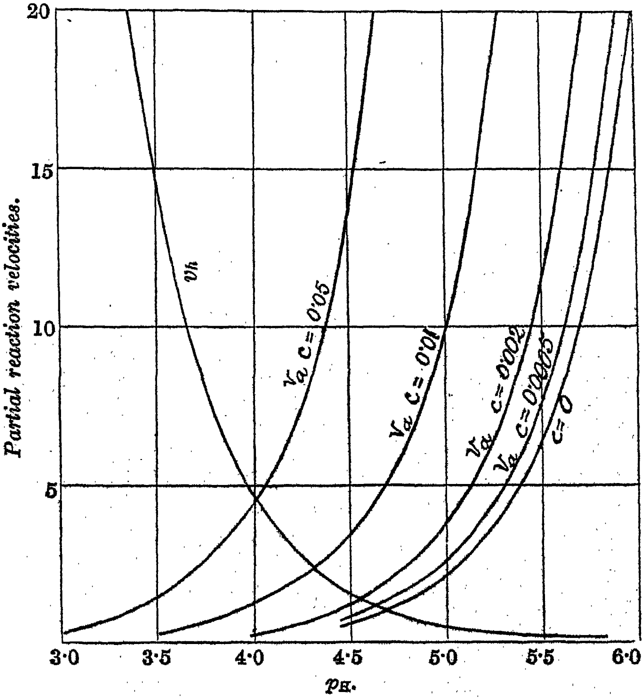
$$v_h = k_h \,.\, 10^{-p_{\mathrm{H}}} \text{ and } v_a = (k_aKc + k_{\mathrm{OH}}K_w)10^{p_{\mathrm{H}}}$$

The curve for v_h and a group of v_a curves for acetic acid concentrations ranging from $c = 0$ to $c = 0{\cdot}05N$ are shown in the diagram and it need only be pointed out that the p_{H} values of the points of intersection of the v_h curve with the several v_a curves are identical with the *M.V.* points of the corresponding catenaries under the conditions which are here postulated.

In regard to the compound catenaries, it should be added that these conform to the requirements of the general catenary in exactly the same way as the simple catenaries. The applicability of the general catalytic catenary is thus further extended to include ionic catalytic effects in which the contribution of the negative ions is shared by anions derived respectively from the solvent and from the acid–salt mixture present in the solution.

The bearing of the above results on the use of buffer mixtures for the study of the velocity of hydrolytic reactions is obvious. The minimum velocities observed under such conditions are larger, and the p_H values smaller than those which would correspond with the *M.V.* point characteristic of the undisturbed action of the hydrogen and hydroxyl ions. In this connexion, it may be noted that since the buffer acid is weak (k_m negligible in comparison with k_h), equations (10) and (11) give $u_i/[H^+]_i = 2k_h$, which is identical with equation (3). It must be remembered, however, that the ionic reaction velocity u_i is not directly measurable. On the assumption that the undissociated water molecules have no measurable activity, the ionic reaction velocity is derived from $u_i = v_i - k_m c$, which requires a knowledge of the catalytic activity of the undissociated buffer acid.

FIG. 1.



Plot of partial velocities due to the hydrogen ion (v_h) and the acetate + hydroxyl ions (v_a) against p_H.

In the circumstances outlined above, it is apparent that the observations made by Karlsson (*Z. anorg. Chem.*, 1921, **119**, 69; 1925, **145**, 1) and Bolin (*ibid.*, 1925, **143**, 201) do not yield either

$(p_H)_i$ values or minimum reaction velocities which can be utilised directly for the derivation of k_h or k_{OH} with any approach to accuracy.

Notwithstanding the approximate character of the $(p_H)_i$ values recorded by Karlsson and Bolin, their data serve to show that the ratio k_{OH}/k_h varies enormously with the nature of the catalysed reaction. The values obtained from the logarithmic equivalent of equation (5), *viz.*,

$$\log k_{OH}/k_h = -\log K_w - 2(p_H)_i,$$

are shown in the fifth column of Table II. Column 1 shows the hydrolyte, col. 2 the temperature of the velocity measurements, col. 3 the ionisation product of water at this temperature, and col. 4 the $(p_H)_i$ values recorded by the above observers.

TABLE II.

Hydrolyte.	Temp.	$K_w \times 10^{14}$.	$(p_H)_i$.	k_{OH}/k_h.
Methyl acetate	25°	1·0	5·15	5,000
Ethyl acetate	25	1·0	5·36	1,900
Glycerol monoacetate	25	1·0	5·0	10,000
Ethyl chloroacetate	20	0·8	4·8	32,000
Ethyl formate	20	0·8	4·65	63,000
Ethyl aminoacetate	20	0·8	3·5	12×10^6
Acetanilide	40	4·0	5·80	63
Benzamide	80	25	6·2	1·6

The value of $(p_H)_i$ given for methyl acetate is that derived by Karlsson (*loc. cit.*, p. 31) from the plot of the logarithm of the observed velocity against p_H; this would seem to be more accurate than the lower value indicated by the v–p_H curve.

For the first five hydrolytes, for which the recorded $(p_H)_i$ values were obtained directly from experiments with buffer solutions, it is probable that the values of k_{OH}/k_h are too large on account of the disturbing influence of the buffer acid and salt. Some indication of the magnitude of this disturbance is obtained when it is pointed out that the correct value of k_{OH}/k_h for ethyl acetate is about 1000. The $(p_H)_i$ values recorded by Bolin for acetanilide and benzamide were derived on the assumption that the acid and alkaline branches of the v–p_H curve are symmetrical with respect to the point of minimum reaction velocity. This empirical assumption is entirely in agreement with the theoretical conclusion reached by Dawson and Dean (J., 1926, 2872) that the p_H value of the *M.V.* point is the arithmetic mean of the p_H values for pairs of solutions of the series $c\text{HA} + x\text{MA}$ which have the same catalytic power.

The application of the isocatalytic method to the systematic determination of the ratio k_{OH}/k_h by the rational use of buffer solutions should make it possible to extend the number of reactions for which this ratio can be derived and thus provide material for the investigation of the question of the mode of action of the hydrogen and hydroxyl ions as catalytic agents in so-called hydrolytic reactions.

Summary.

It is shown that the velocity coefficients k_h and k_{OH} can be derived from the isocatalytic data v_i and $[H^+]_i$.

Approximate values of v_i and $[H^+]_i$ may be obtained by the use of buffer solutions, but the experimental data, which indicate that k_{OH}/k_h varies with the hydrolyte between very wide limits, must be corrected for the catalytic effects which are produced by constituents of the buffer solutions other than the hydrogen and hydroxyl ions.

The curves obtained by plotting the reaction velocity against the p_H value of a series of buffer solutions, in which the concentration of the acid is constant, are catenary in type. These catenary curves are compound in character in that the anionic catalytic effect is shared by the hydroxyl ion and by the anion of the acid in the buffer mixture.

The compound catenaries form a continuous series limited on the one hand by the H^+–OH^- catenary, and on the other by the simple H^+–A^- catenaries corresponding with the mixtures $cHA + xMA$.

The compound catenaries conform to the requirements of the general catalytic catenary, the application of which is thus extended to include anionic catalytic effects which are shared by the hydroxyl ion with other acid anions.

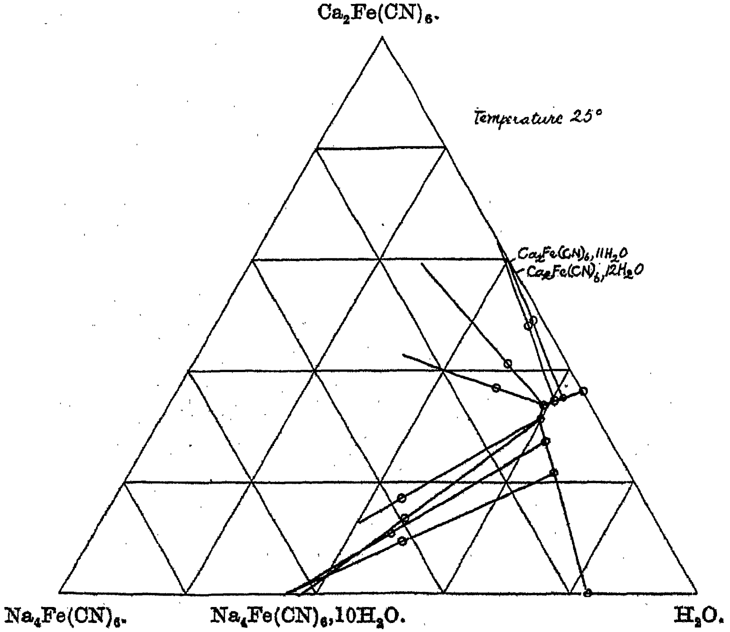
THE UNIVERSITY, LEEDS. [*Received, March 17th, 1927.*]

CLX.—*The System Calcium Ferrocyanide–Sodium Ferrocyanide–Water. Part II.*

By MONICA FARROW.

THE solubility equilibria of the systems calcium ferrocyanide–water and sodium ferrocyanide–water were described by the author in a previous paper (J., 1926, 49), in which it was shown that $Na_4Fe(CN)_6,10H_2O$ undergoes transformation into a less hydrated form at 81·5°. The present paper deals with the three-component system calcium ferrocyanide–sodium ferrocyanide–water, which was investigated with the view of determining by the "Rest" method the formula of the sodium salt which is stable at higher temperatures. This object was not attained, as the two ferrocyanides gave the double salt $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$. This salt, which is of the same type as the well-known double salts of calcium and potassium or ammonium ferrocyanides, has been obtained by Wyrouboff (*Ann. Chim.*, 1870, **21**, 283) by crystallisation from solutions of the mixed components, but the product so prepared was evidently not pure, since Wyrouboff's analyses led him to formulate it as $CaNa_3Fe(CN)_6$. Crystals of the double salt now obtained have been examined by Dr. T. V. Barker, who finds that their crystallographic properties agree with those stated by Wyrouboff.

FIG. 1.



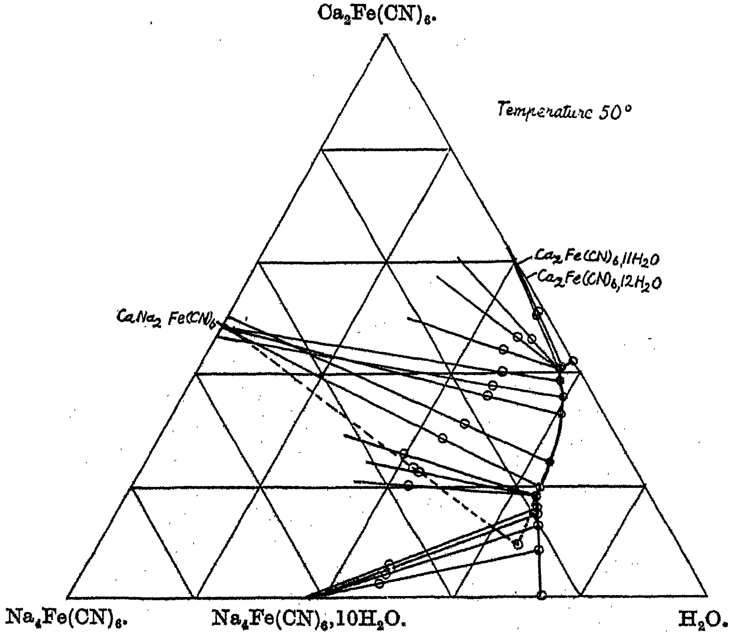
Nevertheless, the system was of some interest and was investigated in detail. The range of the solubility determinations of the calcium salt was extended from the cryohydrate to 90°, and it was found, like the sodium salt, to suffer transformation to a lower state of hydration.

EXPERIMENTAL.

System Calcium Ferrocyanide–Water.

Determination of the solubility of the pure calcium salt at 90° gave 44·2 g. of anhydrous salt per 100 g. of solution, a value almost identical with that obtained at 65°, *viz.*, 44·4 g. In the course of the former experiments five independent determinations of the solubility at 80° were made, giving a mean value of 44·0. These experiments clearly indicate a change of the ordinary hydrate into a form which is stable at higher temperatures and the solubility of which is practically independent of temperature. From cooling curves it appears that the lower limit of stability of the new form is 59·7°. The complete solubility curve of calcium ferrocyanide is now given from —11·6° to 90° as g. of anhydrous salt in 100 g. of solution.

FIG. 2.



Temp. ...	—10·1°	24·9°	34·9°	49·8°	59·7°	64·7°	79·6° & 90°
Conc. ...	30·45	36·44	39·22	42·04	44·20	44·44	44·37

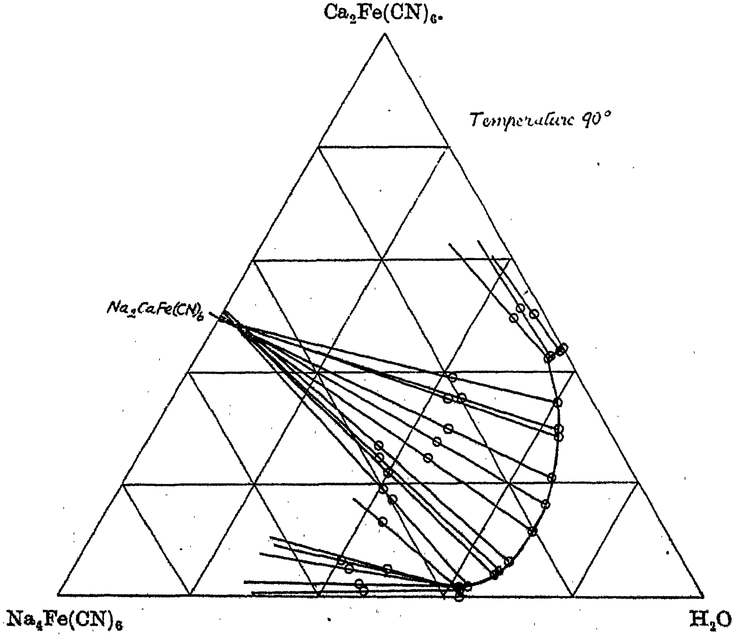
System Calcium Ferrocyanide–Sodium Ferrocyanide–Water.

The composition of the solutions and of the wet solids in equilibrium with them were determined by the methods previously described in detail (*loc. cit.*), *viz.*, the total ferrocyanide by permanganate, and the calcium volumetrically by the oxalate method. The withdrawal of solutions by means of the weight pipette previously described enabled density as well as solubility determinations to be made. The experiments were carried out at 25°, 50°, and 90°, and the results obtained are in the following tables, and represented in Figs. 1, 2, and 3. The values represent weights of anhydrous salt per 100 g. of solution in columns 2 and 3, and per 100 g. of wet solid in columns 5 and 6. The triple-point values are starred. (*M* represents metastable state.)

Determination of Invariant Points.

1. The transition point of pure calcium ferrocyanide was found by means of cooling curves to be 59·7°, and in the presence of the solid double salt to be 58·2°. The solubility of the pure salt was 44·2 g. in 100 g. of solution.

FIG. 3.



2. The transition point of pure sodium ferrocyanide, determined by the same method, was 81·5°, and when the solid double salt was present, it was 81·16°. The composition of the solution at the former temperature was 37·5 g. of $Ca_2Fe(CN)_6$ in 100 g. of solution, and at the latter 3·14 g. of $Ca_2Fe(CN)_6$, 34·74 g. of $Na_4Fe(CN)_6$, and 62·14 g. of water.

3. The melting point of the calcium ferrocyanide cryohydrate was found to be −10·1° and its composition was 30·45 g. of anhydrous salt per 100 g. of solution, which had *d* 1·198.

	Solutions.			Solids.		
D.	$Ca_2Fe(CN)_6$.	$Na_4Fe(CN)_6$.	H_2O.	$Ca_2Fe(CN)_6$.	$Na_4Fe(CN)_6$.	H_2O.
At 25°.						
1·356	37·16	—	62·84	—	—	—
1·369	35·27	3·67	61·05	49·00	1·23	49·76
1·373	35·10	4·79	60·11	48·71	3·01	48·33
* 1·381	33·24	7·55	59·21	42·22	9·55	48·24
-	33·40	7·33	59·27	37·76	14·66	47·60
* —	31·30	8·46	60·24	17·31	37·37	45·27
—	31·60	8·75	59·65	13·97	38·25	47·71
1·344	28·02	9·64	62·34	11·40	42·26	46·41
—	22·22	11·50	66·27	9·88	41·76	48·38
1·130	—	17·04	82·96	—	—	—
At 50°.						
1·392	42·20	—	58·00	—	—	—
—	40·71	2·53	56·78	50·51	1·42	48·08
—	40·51	2·91	56·58	49·30	1·83	49·90
* 1·436	39·95	2·65	57·38	46·46	6·54	46·98
1·438	40·10	2·91	57·00	43·98	9·85	46·17
—	38·70	3·30	57·94	40·10	11·31	48·61
—	36·07	4·73	59·20	37·79	14·65	47·59
1·363	33·08	6·50	60·44	36·63	15·90	47·46
1·332	24·40	12·99	62·61	32·07	23·11	44·81
1·314	20·05	16·24	63·71	29·45	27·73	42·83
1·308	17·28	18·49	64·24	26·32	31·20	42·46
1·311	18·13	18·00	63·87	23·39	34·04	42·51
1·310	17·93	18·44	63·62	20·58	37·22	42·22
M 1·280	9·53	25·25	65·26	23·88	34·18	41·91
1·300	16·26	18·65	65·10	6·09	47·17	46·79
1·296	15·57	19·37	65·52	5·71	47·38	46·96
1·281	13·18	20·10	66·74	4·59	48·41	47·01
1·255	9·13	22·11	68·76	3·01	49·61	47·38
1·200	—	26·20	73·80	—	—	—
At 90°.						
1·401	44·40	—	55·60	—	—	—
1·400	43·96	0·34	55·70	50·35	1·71	47·88
1·396	42·74	2·77	54·50	50·81	2·99	46·20
* —	42·42	3·12	54·44	49·16	4·47	46·37
1·335	34·74	5·02	60·27	39·05	19·22	41·73
1·313	30·17	7·43	62·39	35·52	19·90	44·57
1·307	29·09	8·08	62·82	35·66	22·55	41·80
1·307	21·34	13·09	65·56	30·27	25·50	44·26
1·249	16·64	16·28	67·07	28·32	28·21	43·56
—	14·88	18·18	66·94	27·40	29·73	42·86
1·238	11·99	20·29	67·71	25·50	31·15	43·36
1·238	11·44	20·49	68·13	23·56	29·52	46·90
1·242	6·54	26·83	66·61	25·94	35·85	38·20
1·240	6·49	26·72	66·67	29·03	37·10	33·89
1·252	4·88	29·48	65·53	25·60	37·79	36·62
1·256	3·83	31·36	64·97	23·33	39·02	37·64
1·266	2·89	33·55	63·59	21·47	38·35	40·19
1·279	2·20	35·36	62·46	19·08	40·36	40·56
1·284	2·21	35·77	62·02	17·45	39·81	42·73
1·302	1·46	38·97	59·58	13·97	43·54	42·47
* 1·285	1·88	37·04	61·05	6·87	53·15	39·95
1·285	1·81	36·81	61·38	5·63	47·55	46·81
1·288	1·72	36·97	61·31	2·41	52·52	45·03
1·288	1·37	37·35	38·73	1·30	54·55	44·13
1·290	—	38·00	62·00	—	—	—

4. The cryohydric temperature of sodium ferrocyanide was estimated as —1·40° and the concentration as 6·81 g. in 100 g. of solution. The density, by extrapolation, is 1·130.

5. The cryohydric temperature for the three-component system was —11·6°, and the concentrations were $Ca_2Fe(CN)_6$, 28·9; $Na_4Fe(CN)_6$, 3·587; H_2O, 67·51%.

Discussion.

At all three temperatures investigated, the double salt is stable, and the range of stability increases markedly with rise in temperature. The range of solutions in equilibrium with the double salt $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$ moves over very much towards the calcium side at lower temperatures. The solubility curve for the double salt is continued into the metastable region at 50° as shown in the diagram.

The values obtained at 25° and 50° confirm the accepted formula of the sodium salt as $Na_4Fe(CN)_6,10H_2O$, and provide additional evidence that the formula of the calcium salt is $Ca_2Fe(CN)_6,11H_2O$ and not $Ca_2Fe(CN)_6,12H_2O$, as might be expected. The evidence at 90° is less satisfactory, as the range of solutions with which the simple salt is in equilibrium is in both cases very limited. The values obtained are sufficient to show that at this temperature the stable forms of the two salts are less highly hydrated than at the lower temperatures, but precise formulation must await the investigation of other systems. Both at 90° and at 50° the tie-lines clearly indicate a formula $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$ for the double salt. At 50°, both the single salts are highly hydrated; the tendency of the double salt to combine with water is thus markedly less than that of the single salts. In its temperature coefficient of solubility it also diverges considerably from the behaviour of the hydrated components, for its solubility clearly falls with increase in temperature. This fact is also probably connected with the absence of hydration, since the dehydrated forms of the single salts have no appreciable temperature coefficient of solubility.

The author would like to express her thanks to Mr. M. P. Applebey for much valuable advice and criticism during the course of the work, and to Dr. T. V. Barker, Reader in Crystallography, for the crystallographic measurements of the calcium–sodium double salt.

UNIVERSITY MUSEUM, OXFORD. [*Received, March 24th,* 1927.]

CLXI.—*The Interaction of Alkali Sulphites with some Halogeno-compounds, and the Optical Resolution of α-Phenylpropanesulphonic Acid.*

By Eric Bertram Evans, Ernest Edward Mabbott, and Eustace Ebenezer Turner.

The original object of this work was to determine whether the interaction of sodium sulphite and asymmetric halogen compounds of the type CHRR′X would afford a practicable method for the preparation of some optically resolvable sulphonic acids required for another investigation. We have, however, not been concerned with the sulpho-carboxylic acids, which have been simultaneously investigated by Backer and Burgers (see, for example, J., 1925, **127**, 233).

Cohen and Clutterbuck (J., 1923, **123**, 2507) stated that β-phenylethyl chloride was converted by boiling aqueous sodium sulphite into styrene, with evolution of sulphur dioxide. We find, however, that the chloride is converted under these conditions into a mixture of *sodium* β-*phenylethanesulphonate*, $CH_2Ph\cdot CH_2\cdot SO_3Na$ (65% yield), and β-phenylethyl alcohol, no appreciable evolution of sulphur dioxide occurring. Sodium or potassium sulphite converts β-phenylethyl bromide even more rapidly and completely into sulphonate.

β-*Phenylethanesulphonyl chloride* and the corresponding *amide* and *anilide* are readily obtainable from the sodium sulphonate. The isolation of the amide makes it possible to cite the series $Ph\cdot[CH_2]_x\cdot SO_2\cdot NH_2$ as another in which there is an alternation in melting point (compare Roberts, Turner, and Bury, J., 1926, 1443): for $x = 0, 1, 2,$ and 3, the m. p.'s are respectively 153°, 105°, 119°, and 35°.

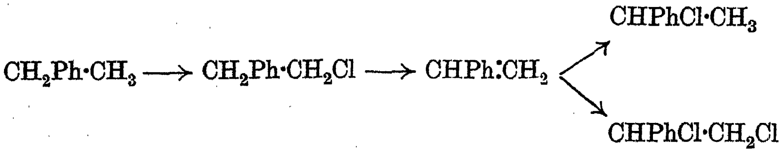
Similarly, α-phenylethyl chloride (bromide) reacts with boiling aqueous sodium sulphite to give *sodium* α-*phenylethanesulphonate*, $CHPhMe\cdot SO_3Na$ (yield, 43—45%). Considerable evolution of sulphur dioxide occurs and some styrene is formed.

Fittig and Kiesow (*Annalen*, 1870, **156**, 246) and, later, Anschütz (*ibid.*, 1886, **235**, 329) concluded that chlorination of boiling ethylbenzene afforded mainly β-phenylethyl chloride, whilst Schramm (*Monatsh.*, 1887, **8**, 102; *Ber.*, 1893, **26**, 1706) obtained a mixture of the α- and β-chlorides. We find that pure ethylbenzene, prepared from acetophenone (Clemmensen, *Ber.*, 1913, **46**, 1840), chlorinates readily in diffused daylight to give (corresponding to monochlorination) a mixture of α- and β-phenylethyl chlorides with higher-boiling material (αβ-dichlorophenylethane, etc.), increased illumination appearing to augment the proportion of α-chloride.

When the contained α- and β-chloride mixture is boiled with aqueous sodium sulphite, it gives rise to appreciable quantities of sulphur dioxide and styrene, but at the same time to a mixture of the corresponding sodium sulphonates.

Dimethylaniline is indifferent towards β-phenylethyl chloride, but combines with the α-chloride to give the crystalline *phenyl-α-phenylethyldimethylammonium chloride*, $CHPhMe{\cdot}NPhMe_2Cl$. When a mixture, with dimethylaniline, of the above purified chlorination mixture was kept for several months, it deposited no solid, a fact which shows that the mixture was predominatingly β-chloride.

The chlorination of ethylbenzene probably gives, as the first product, mainly β-phenylethyl chloride, but the decomposition of this substance, during the chlorination process, produces styrene, which combines either with hydrogen chloride or with chlorine :



$$\begin{tikzcd}[column sep=small] & & & CHPhCl{\cdot}CH_3 \\ CH_2Ph{\cdot}CH_3 \arrow[r] & CH_2Ph{\cdot}CH_2Cl \arrow[r] & CHPh{:}CH_2 \arrow[ur] \arrow[dr] & \\ & & & CHPhCl{\cdot}CH_2Cl \end{tikzcd}$$

When *strychnine* dl-*α-phenylethanesulphonate* was crystallised from water, *strychnine* l-*α-phenylethanesulphonate* separated first.

As considerable quantities of phenylmethylcarbinol were required for this work, we re-examined the reduction of acetophenone, using sodium and moist ether–toluene. The main product was, however, αβ-diphenyl-αβ-dimethylethane-αβ-diol (acetophenone pinacol). This is therefore, apparently, the best way of obtaining this substance, since in 1917 (*J. Amer. Chem. Soc.*, **39**, 291) Johlin, who investigated various methods for its preparation, including the reduction of acetophenone by other processes, concluded that it was then most conveniently prepared from magnesium methyl iodide and benzil.

α-Phenylpropyl bromide also reacted with boiling aqueous sodium sulphite, but only about 10% was converted into *sodium α-phenylpropanesulphonate*, $CHPhEt{\cdot}SO_3Na$. Prolonged shaking of the reactants at the ordinary temperature, however, gave a 30% yield. When an aqueous solution of *α-phenylpropanesulphonic acid* was treated with half an equivalent of strychnine, it afforded the sparingly soluble *strychnine* d-*α-phenylpropanesulphonate* with $[\alpha]_D^{25^\circ}$ $-$ 23·7° ; the mother-liquor gave, with cinchonine, the l-*α-phenylpropanesulphonate* of the latter base, having $[\alpha]_D^{25^\circ}$ + 104·9°. From the two alkaloidal salts were obtained the two *sodium* salts, with $[\alpha]_D^{25^\circ}$ + 5·2° and $-$ 5·2°, respectively.

α-Phenylbutyl bromide reacted slowly with aqueous sodium sulphite at the ordinary temperature to give a little *sodium α-phenylbutane-*

sulphonate, $CHPhPr^{\alpha}\cdot SO_3Na$, the majority of the bromo-compound, however, being converted into α-phenyl-Δ^{α}-butene.

In other experiments designed to provide α-phenylbutanesulphonic acid, magnesium α-phenylbutyl bromide was found to react with sulphur dioxide to give, instead of the desired sulphinic acid, *di-α-phenylbutyl sulphide* $(PhPr^{\alpha}CH)_2S$ (compare Rosenheim and Singer, *Ber.*, 1904, **37**, 2152; Oddo, *Gazzetta*, 1911, **41**, 11).

The effect upon the conversion of α-phenylethyl halides into sodium sulphonates, of negative substituents in the benzene ring was also tested. 2 : 4-Dichloroiodobenzene (Ullmann, *Annalen*, 1904, **332**, 38) combined with magnesium to give magnesium 2 : 4-dichlorophenyl iodide, and this reacted with acetaldehyde to give 2 : *4-dichlorophenylmethylcarbinol*. No difficulty was experienced in converting this substance into the corresponding *bromide*, but when the latter was treated with boiling aqueous sodium sulphite, it was almost quantitatively converted into the carbinol. This result is somewhat similar to that observed by Wedekind and Schenk (*Ber.*, 1911, **44**, 198) with diphenylhalogenomethanes, when the corresponding ether was formed as the only product. No 2 : 4-dichlorostyrene was produced in the above reaction, this fact and the above formation of carbinol being apparently due to the negative effect of the ortho-para chlorine atoms. Again, α-2 : 4-dichlorophenylethyl bromide is devoid of lachrymatory properties, unlike α-phenylethyl bromide itself.

β-Bromobutane, readily obtainable from methyl ethyl ketone (Bentley, J., 1895, **67**, 264; Norris, Green, and Johnson, *Amer. Chem. J.*, 1901, **26**, 293), reacted at a convenient rate with warm aqueous sodium sulphite to give over half the calculated quantity of *sodium α-methylpropanesulphonate*, $CHMeEt\cdot SO_3Na$. *Strychnine* d-*α-methylpropanesulphonate* is less soluble in water than its diastereoisomeride. No other alkaloidal salt could be obtained crystalline.

EXPERIMENTAL.

Sodium β-Phenylethanesulphonate.—(a) *From β-phenylethyl chloride.* A mixture of 20 g. of the chloride with a saturated aqueous solution of 40 g. of sodium sulphite heptahydrate was heated to boiling for 20 hours; 4 g. of oil, identified as β-phenylethyl alcohol, remained undissolved. No sulphur dioxide evolution was observed during the process. The cooled reaction mixture deposited a mass of crystals which, after crystallisation from water, gave white plates of *sodium β-phenylethanesulphonate* (yield, 65%) (Found: Na, 11·1. $C_8H_9O_3SNa$ requires Na, 11·1%). (b) *From β-phenylethyl bromide.* A mixture of 37 g. of the bromide and a saturated solution of 55 g. of sodium sulphite was boiled under reflux. Crystals began to form in the boiling solution after 2·5 hours, and in 3 hours the bromide had disappeared. On cooling, the liquid set to a crystalline mass, which was filtered off. The solid was crystallised from water, a 90% yield of the sodium sulphonate being obtained (Found: Na, 11·2%).

The *potassium* salt was obtained similarly, and separated from water in white plates (yield, 90%) (Found: K, 17·3. $C_8H_9O_3SK$ requires K, 17·4%). The *barium* salt was precipitated when concentrated solutions of barium chloride and of the above sodium salt were mixed. Recrystallised from water, it formed small leaflets (Found: Ba, 27·2. $C_{16}H_{18}O_6S_2Ba$ requires Ba, 27·0%).

β-*Phenylethanesulphonic acid*, obtained from the barium salt and an equivalent of sulphuric acid, crystallised from very concentrated solutions in small, deliquescent leaflets, m. p. 91°. After being left in contact with porous porcelain for a short time in a dry atmosphere, it was found to contain 5 mols. of water of crystallisation.

β-*Phenylethanesulphonyl Chloride*.—The sodium salt reacted normally with phosphorus pentachloride to give the *sulphonyl chloride*, which crystallised from light petroleum in white, silky needles, m. p. 34° (Found: Cl, 17·6. $C_8H_9O_2ClS$ requires Cl, 17·4%).

β-*Phenylethanesulphonamide* was obtained by passing dry ammonia into a well-cooled ethereal solution of the chloride. It separated from water in white plates, m. p. 119° (Found: N, 7·3. $C_8H_{11}O_2NS$ requires N, 7·6%). The chloride reacted readily in ethereal solution with aniline, giving the *anilide*, which crystallised from aqueous alcohol in white needles, m. p. 77° (Found: N, 5·2. $C_{14}H_{15}O_2NS$ requires N, 5·4%).

Sodium α-Phenylethanesulphonate.—A mixture of 40 g. of α-phenylethyl bromide and a saturated solution of 60 g. of sodium sulphite was boiled under reflux. A brisk evolution of sulphur dioxide occurred, and the layer of organic liquid, at first at the bottom, rose to the top. When, after 6 hours' boiling, no more sulphur dioxide was evolved, the liquid was cooled. The top layer consisted of styrene (10 g.), and the aqueous layer, after being evaporated to about two-thirds of its original bulk, deposited white plates on cooling. These were crystallised from water (yield, 45%) (Found: Na, 11·1. $C_8H_9O_3SNa$ requires Na, 11·1%).

When 100 g. of α-phenylethyl bromide was used for this preparation, only 10 g. of sulphonate were obtained; the use of small quantities is therefore to be recommended.

With α-phenylethyl chloride (30 g.) instead of the bromide, the reaction was complete in 9 hours, and a 43% yield of sodium salt was obtained.

Barium α-phenylethanesulphonate crystallised in long needles when a solution containing the sodium salt and the calculated quantity of barium chloride was cooled (Found: Ba, 27·3. $C_{16}H_{18}O_6S_2Ba$ requires Ba, 27·0%). The *potassium* salt, obtained from the barium salt and potassium sulphate, crystallised from water in plates (Found: K, 17·5. $C_8H_9O_3SK$ requires K, 17·4%).

α-Phenylethanesulphonyl chloride, formed from the sodium salt in the usual manner, separated from alcohol in small, white needles, m. p. 79° (Found: Cl, 17·5. $C_8H_9O_2ClS$ requires Cl, 17·4%).

Chlorination of Ethylbenzene.—When chlorine was passed into boiling ethylbenzene in bright sunlight (Sydney, N.S.W.), chlorination was very rapid and gave a mixture of polychloro-derivatives. Dry chlorine was passed for 4 hours into 30·7 g. of boiling ethylbenzene in bright sunlight (London) until an increase of 9 g. in weight occurred. The product separated when distilled into three fractions: (1) b. p. up to 82°/15 mm., 2 g.; (2) b. p. 82—100°/15 mm., 16 g.; and (3) b. p. 100—125°/15 mm., 12 g. Fraction (2) was boiled with sodium sulphite solution. Sulphur dioxide was evolved, and after 8 hours the solution was cooled; crystals of the sulphonate mixture then separated and 2 g. of styrene were isolated. Fraction (3) was rich in αβ-dichlorophenylethane.

A second chlorination of 43 g. of ethylbenzene, carried out on a very dull day, lasted 9 hours. The product was separated into 3 fractions: (1) b. p. up to 82°/15 mm., 3 g.; (2) b. p. 82—102°/15 mm., 20 g.; and (3) b. p. 102—120°/15 mm., 20 g. Fraction (2), the greater portion of which distilled at 90—100°/15 mm., was only slightly lachrymatory and was evidently mainly β-phenylethyl chloride; for, when it was heated with sodium sulphite, it gave rise to very little sulphur dioxide and styrene, and a good yield of sulphonate.

Equimolecular mixtures, with dimethylaniline, of α- and β-phenylethyl chlorides and fraction (2) of the last chlorination were allowed to remain at the ordinary temperature for 5 months. The mixture containing the α-chloride became almost solid. The product was left in contact with porous porcelain in a dry atmosphere, and then became a colourless, crystalline mass of *phenyl-α-phenylethyldimethylammonium chloride*, m. p. 95° (Found: Cl, 13·6. $C_{16}H_{20}NCl$ requires Cl, 13·6%). The other two mixtures deposited no solid.

Strychnine dl-*α-Phenylethanesulphonate.*—To a boiling aqueous solution of barium α-phenylethanesulphonate (21·99 g.) was added a boiling solution of 29 g. of strychnine in the equivalent quantity of *N*-sulphuric acid. The barium sulphate was collected, and the filtrate was evaporated almost to dryness. The solid so obtained was analysed (Found: N, 5·6. $C_{21}H_{22}O_2N_2,C_8H_{10}O_3S$ requires N, 5·4%).

Fractional crystallisation of this racemate gave *strychnine* l-*α-phenylethanesulphonate* as the less soluble salt. A 1·874% solution in 50% aqueous alcohol had $\alpha_{D}^{18^\circ} - 0{\cdot}81^\circ$ (2-dcm. tube), whence $[\alpha]_{D}^{18^\circ} - 20{\cdot}5^\circ$.

Similarly, when a hot solution of 4·62 g. of sodium α-phenylethanesulphonate was treated with a hot solution of 3·71 g. of strychnine (dissolved in an equivalent of *N*-sulphuric acid), and the solution allowed to cool, pure strychnine *l*-sulphonate separated, having $[\alpha]_{D}^{18^\circ} - 20{\cdot}5^\circ$.

Potassium l-*α-phenylethanesulphonate* was obtained by treating the strychnine salt with potassium carbonate. A 1·90% solution in water had $\alpha_{D}^{18^\circ} - 0{\cdot}45^\circ$ ($l = 2$ dcm.), whence $[\alpha]_{D}^{18^\circ} - 11{\cdot}8^\circ$.

Systematic treatment of the mother-liquors from the strychnine *l*-sulphonate did not afford a pure *d*-sulphonate.

Brucine dl-*α-phenylethanesulphonate* was obtained crystalline only after a great deal of preliminary treatment. It was very soluble in water, alcohol, ether, carbon tetrachloride, and acetone, though sparingly soluble in benzene, and could not be caused to crystallise systematically (Found: N, 5·1. $C_{23}H_{26}O_4N_2,C_8H_{10}O_3S$ requires N, 4·8%). *Cinchonidine* dl-*α-phenylethanesulphonate* was even more difficult to obtain crystalline, and could not be fractionally crystallised, being very soluble in most solvents (Found: N, 4·4. $C_{27}H_{32}O_4N_2,C_8H_{10}O_3S$ requires N, 4·2%).

Preparation of αβ-Diphenyl-αβ-dimethylethane-αβ-diol.—A solution of acetophenone (60 g.) in moist ether (150 c.c.) was slowly added to 46 g. of powdered sodium covered with 100 g. of toluene. Water was then added gradually. After a time, the whole became practically solid. Water was added until the solid redissolved, the ether–toluene layer then being removed, washed, dried and distilled, until the residue was at 150°. On cooling, it solidified, and after several crystallisations from alcohol and benzene melted at 121° (Found: *M*, cryoscopic in benzene, 232, 251. Calc.: *M*, 242).

Preparation of 2 : 4-*Dichlorophenylmethylcarbinol.*—2 : 4-Dichloroiodobenzene (68 g.; b. p. 255—257° [Ullmann, *Annalen*, 1904, **332**, 38, gives 262—263°]; obtained from 2 : 4-dichloroaniline), when dissolved in ether, combined readily with magnesium (6 g.) in presence of a little iodine. The solution was treated gradually with an ethereal solution of 16 g. of acetaldehyde. The mixture was left over-night and then treated with ice and dilute hydrochloric acid, and the ethereal solution was washed with aqueous sodium hydrogen carbonate, with aqueous sodium hydrogen sulphite, and with sodium hydrogen carbonate. It was then dried; the carbinol, by distillation under diminished pressure, was obtained as a pale yellow liquid, b. p. 145°/20 mm., or 154—155°/29 mm. (yield 67%) (Found: Cl, 38·5. $C_8H_8OCl_2$ requires Cl, 37·2%).

α-2 : 4-*Dichlorophenylethyl Bromide.*—Hydrogen bromide was passed into the carbinol for 4 hours, and the product was treated with dilute sodium carbonate solution, then with water, and finally distilled under diminished pressure. The bromide was obtained as a mobile, colourless liquid, b. p. 154°/37 mm., with hardly any odour or lachrymatory properties (Found: AgCl + AgBr, 0·3350. $C_8H_7Cl_2Br$ requires AgCl + AgBr, 0·3418).

Action of Sodium Sulphite on α-2 : 4-*Dichlorophenylethyl Bromide.*—The bromide (10 g.) was heated with a solution of sodium sulphite for 30 hours; 7 g. of the carbinol (calc., 7·5 g.) were then obtained, b. p. 154°/29 mm.

Preparation of 3 : 5-*Dichlorobromobenzene.*—When 2 : 4-dichloroacetanilide was brominated in glacial acetic acid solution, it was converted into slightly more than its own weight of 2 : 4-dichloro-6-bromoaniline, m. p. 81°, the acetyl group being eliminated in the process. Treatment of the base with sodium nitrite, alcohol, benzene and concentrated sulphuric acid in the usual manner gave a 38% yield of 3 : 5-dichlorobromobenzene. This substance, after several crystallisations from alcohol, melted at 74°, although Hartley (J., 1901, **79**, 1293) gives 77·5°, and Hantzsch (*Ber.*, 1897, **30**, 2351) gives 82—84°. It reacted with magnesium which had previously been activated with methyl iodide.

Sodium α-*Phenylpropanesulphonate.*—α-Phenylpropyl bromide (15 g.) was heated in the usual manner with sodium sulphite solution. Propenylbenzene was the main product, only 2 g. of impure sulphonate being obtained. Ammonium sulphite gave similar results.

The bromide (90 g.) was shaken vigorously for 120 hours with a solution of 120 g. of sodium sulphite heptahydrate in 240 c.c. of water. After several hours' shaking, crystals began to separate, and when no further change was apparent the solid was collected and the oily layer separated (35 g.). The solid was freed from bromide and sulphite by systematic crystallisation from water, and ultimately gave 30 g. (30% yield) of pure sodium α-phenylpropanesulphonate, very soluble in water, but almost insoluble in alcohol (Found: Na, 10·4. $C_9H_{11}O_3SNa$ requires Na, 10·4%).

In a second experiment, 60 g. of bromide gave 21 g. (32% yield) of sulphonate and 23 g. of oil. From the density of the latter it was estimated that it contained about 6 g. of unchanged bromide and 17 g. of propenylbenzene. This indicates that, in the above experiment, about 50% of the bromide underwent loss of hydrogen bromide.

α-*Phenylpropanesulphonic Acid.*—Addition of barium chloride solution to one of the sodium sulphonate caused the precipitation of a mixture of salts which could not be separated. The free acid was therefore prepared as follows : A hot concentrated solution of the sodium salt was treated with an excess of concentrated hydrochloric acid, and the sodium chloride removed. The liquid was evaporated, and the whole process repeated four times; on final evaporation, the sulphonic acid was obtained as a deliquescent, gummy solid which partly crystallised on desiccation for some weeks, but could not be recrystallised from a solvent.

α-Phenylpropanesulphonyl chloride was obtained from the sodium salt and phosphorus pentachloride as a colourless, heavy liquid, b. p. 175°/20 mm. (Found: Cl, 15·9. $C_9H_{11}O_2ClS$ requires Cl, 16·3%). The corresponding *amide* and *anilide* could not be caused to crystallise.

Resolution of dl-*α-Phenylpropanesulphonic Acid.*—Finely powdered strychnine (4·15 g.) was allowed to dissolve in a hot aqueous solution of 5 g. (2 equivs.) of the sulphonic acid. On cooling, the strychnine salt separated, and this, after being recrystallised three times from water, weighed 3 g. (0·1644 g. was equivalent to 3·00 c.c. of 0·1*N*-sodium hydroxide. $C_{21}H_{22}O_2N_2,C_9H_{12}O_3S$ requires 3·10 c.c.). The salt had $[\alpha]_D^{26°}$ — 23·7° in aqueous alcohol (water, 1 vol.; alcohol, 2 vols.), and was unaffected by further recrystallisation.

To the heated mother-liquor remaining after removal of the strychnine salt, 0·5 equivalent (3·7 g.) of cinchonine was added. When further dissolution ceased, a little cinchonine was filtered off, and the filtrate was cooled. The precipitated solid was recrystallised thrice from water; 2·6 g. of *cinchonine* salt were then obtained (0·1184 g. was equivalent to 2·20 c.c. of 0·1*N*-sodium hydroxide. $C_{20}H_{21}O_4N,C_9H_{12}O_3S$ requires 2·40 c.c.). The salt had $[\alpha]_D^{25°}$ + 104·9° in aqueous alcohol, and was not affected by further crystallisation.

The alkaloidal salts were converted into the *sodium* salts by treatment with the calculated quantity of sodium hydrogen carbonate in aqueous solution. That from the strychnine salt had $[\alpha]_D^{25°}$ + 5·2° ± 0·1° (Found: Na, 10·3%). That from the cinchonine salt had $[\alpha]_D^{25°}$ — 5·2° ± 0·2° (Found: Na, 10·4%).

α-Phenylbutyl bromide was obtained by passing hydrogen bromide through phenyl-*n*-propylcarbinol, prepared from benzaldehyde and magnesium *n*-propyl bromide (Grignard, *Ann. Chim. Phys.*, 1901, **24**, 466; Klages, *Ber.*, 1904, **37**, 2312). The bromide was thus obtained as a colourless, lachrymatory liquid, *d* about 1·24, b. p. 116°/28 mm., or 126°/47 mm. (Found: Br, 38·0. $C_{10}H_{13}Br$ requires Br, 37·6%).

Sodium α-Phenylbutanesulphonate.—The bromide (20 g.) was shaken with aqueous sodium sulphite at the ordinary temperature for 135 hours. From the density of the residual oily layer, it was estimated that 60% of the bromide had been converted into α-phenyl-Δ^{α}-butene, 30% had remained unchanged, and 10% had reacted in the desired manner. Only 1·2 g. of sodium salt (yield about 6%) were obtained (Found : Na, 9·6. $C_{10}H_{13}O_3SNa$ requires Na, 9·7%).

Action of Sulphur Dioxide on Magnesium α-Phenylbutyl Bromide.—The Grignard reagent obtained from α-phenylbutyl bromide (5·5 g.) was cooled in ice and salt, and saturated with sulphur dioxide. A white solid separated, but dissolved before the calculated quantity of sulphur dioxide had been used. The resulting yellow solution, when decomposed in the usual manner, gave an ethereal solution which, on evaporation, gave white crystals. These, when recrystallised from alcohol, melted at 96°, and consisted of the *sulphide*, $(PhPr^{\alpha}CH)_2S$ (Found : S, 10·5. $C_{20}H_{26}S$ requires S, 10·7%).

Sodium α-Methylpropanesulphonate.—α-Bromobutane (115 g.) was heated gently under reflux for 100 hours with aqueous sodium sulphite; it had then all disappeared. The solution obtained was evaporated in stages, the crude sulphonate being obtained as the most soluble fraction. Recrystallisation from water gave 65 g. (50% yield) of the *sodium* salt (Found : Na, 14·5. $C_4H_9O_3SNa$ requires Na, 14·4%). The salt forms colourless plates which are very soluble in cold water.

α-Methylpropanesulphonic acid was prepared by repeated evaporation of the sodium salt with hydrochloric acid. It forms colourless, hygroscopic, hexagonal plates. Half an equivalent of strychnine was dissolved in an aqueous-alcoholic solution of the acid. A *strychnine* salt separated on cooling, and this, after being recrystallised thrice from aqueous alcohol, formed white needles sparingly soluble in water, more soluble in aqueous alcohol (Found, by titration against 0·1*N*-NaOH : strychnine, 70·0. $C_{21}H_{22}O_2N_2,C_3H_{10}O_3S$ requires strychnine, 70·7%). A solution of 0·485 g. of the salt in 50 c.c. of 50% aqueous alcohol had $\alpha_{D}^{20^{\circ}} - 0{\cdot}57^{\circ}$ in a 2-dcm. tube, whence $[\alpha]_{D}^{20^{\circ}} - 29{\cdot}3^{\circ}$.

The corresponding sodium salt was only obtained in a very small quantity, and a qualitative examination showed it to be dextrorotatory. The *cinchonine* salt of the acid could not be obtained crystalline.

Sodium sec.-*butyl sulphate* was obtained from methylethylcarbinol *via* the calcium salt, and crystallised from alcohol (Found : Na, 13·0. $C_4H_9O_4SNa$ requires Na, 13·1%).

Part of the investigation of α-methylpropanesulphonic acid and its salts was carried out by Mr. J. F. Shillito, B.Sc., who was responsible for its partial resolution. The authors desire to thank the Research Grant Committee of the Society for grants in aid of this investigation.

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[*Received, March* 10*th*, 1927.]

CLXII.—*The Scission of Diaryl Ethers and Related Compounds by means of Piperidine. Part I. The Scope of the Method and its Use in determining the Constitution of some Nitro-derivatives.*

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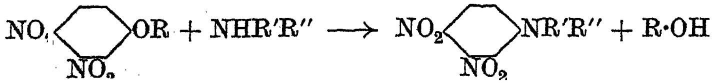
IT has been known for some time that ethers of nitrophenols react with ammonia, and with some of its mono- and di-substitution products, to give an alcohol (phenol) and a nitro-base :



The extent to which substituents affect the course of this reaction is, however, a matter requiring investigation. Further, when R is a substituted aryl group, there is a possibility that a base such as piperidine may, in effecting the scission, which may now be written : $R{\cdot}O{\cdot}R' + C_5H_{10}NH \longrightarrow R{\cdot}NC_5H_{10} + R'{\cdot}OH$, give rise to more than two products. It should be possible, therefore, to use such reactions to compare the effects of different groups, or similar groups in different positions, on the strengths of attachment of the oxygen atom to the two benzene nuclei.

In order to determine the scope of the method, we have first investigated the behaviour towards piperidine of a number of substituted diphenyl ethers, some of which have been prepared for the purpose.

Diphenyl ether itself does not react with piperidine at 100°. 2- and 4-Nitrodiphenyl ether, and 2′-, 3′-, and 4′-chloro-2-nitrodiphenyl ether react slowly with piperidine at this temperature. On the other hand, 2 : 4-dinitrodiphenyl ether (I), 4′-bromo-2 : 4-dinitrodiphenyl ether (II), 2′ : 4′-dibromo-2 : 4-dinitrodiphenyl ether, and 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether give colorations in the cold with piperidine, which at 100° converts them in the course of a few minutes into mixtures of 2 : 4-dinitrophenylpiperidine

(Lellmann and Geller, *Ber.*, 1888, **21**, 2283) (III) and phenol, *p*-bromo-, 2 : 4-dibromo-, and 2 : 4-dinitro-phenol, respectively.

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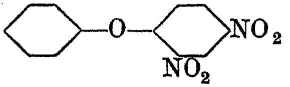

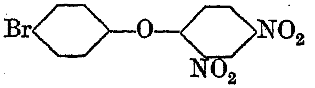

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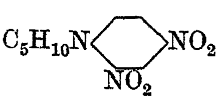

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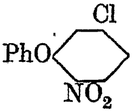

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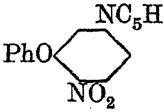

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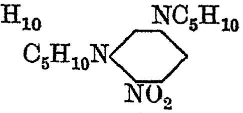
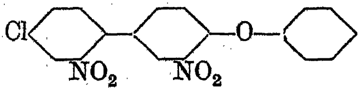


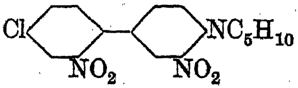
(VI.)

In 5-chloro-2-nitrodiphenyl ether (IV), the chlorine atom is more reactive than the phenoxyl radical, and by adjusting the conditions it is therefore possible to convert the ether first into 5-*piperidino-2-nitrodiphenyl ether* (V) and then into 1-nitro-2 : 4-dipiperidinobenzene (VI).

The considerable reactivity of diaryl ethers is well illustrated by the fact that we now find that 4-chloro-2 : 3′-dinitro-4′-phenoxydiphenyl (VII) and the corresponding 4-bromo-compound, both comparatively complex, are rapidly and quantitatively converted by piperidine at 100° into 4-chloro- (VIII) and 4-bromo-2 : 3′-dinitro-4′-piperidinodiphenyl respectively (compare Dennett and Turner, J., 1926, 476; Le Fèvre and Turner, *ibid.*, p. 1759).



(VII.)



(VIII.)

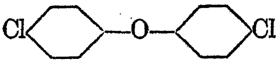
Similarly, 3 : 3′-dinitro-4 : 4′-diphenoxydiphenyl is converted, though apparently more slowly, into 3 : 3′-dinitro-4 : 4′-dipiperidinodiphenyl.

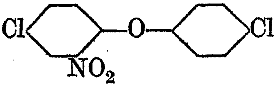
2 : 4-Dinitrodiphenyl ether, when brominated, gave the 4′-bromo-derivative, the constitution of which follows (1) from its synthesis from 1-chloro-2 : 4-dinitrobenzene and potassium *p*-bromophenoxide, and (2) from its conversion, by piperidine, into *p*-bromophenol and 2 : 4-dinitrophenylpiperidine.

Hoffmeister (*Annalen*, 1871, **159**, 210), by the bromination of diphenyl ether, obtained a dibromo-derivative, m. p. 53—55°, which was regarded by Mailhe and Murat (*Bull. Soc. chim.*, 1912, **11**, 33), without supporting experimental evidence, as the 4 : 4′-compound. This constitution for the substance has now been established by synthesis. 4-Bromo-4′-nitrodiphenyl ether, obtained from potassium *p*-bromophenoxide and *p*-chloronitrobenzene, on reduction gave 4-*bromo*-4′-*aminodiphenyl ether*, from which the 4 : 4′-dibromo-derivative was readily prepared. It melted at 60·5°, but repetition of Hoffmeister's experiments gave an identical substance.

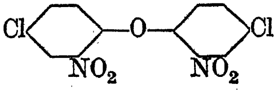
4 : 4′-Dichlorodiphenyl ether (IX), synthesised in a similar manner, was converted by excess of cold fuming nitric acid into a dinitro-compound. The latter was shown to be (XI), since it reacted with piperidine to give a mixture of 4-chloro-2-nitrophenol and 4-chloro-2-nitropiperidinobenzene.

(IX.)





(X.)



(XI.)

Mononitration of the dichlorodiphenyl ether was also effected, and the product (X), when further nitrated, was quantitatively converted into (XI). No 3-nitration appears to occur, demonstrating again that oxygen has a much greater directive influence than chlorine (compare the nitration of *o*-fluoroanisole by Holmes and Ingold, J., 1926, 1328). The present experiments incidentally establish the constitution of the product of direct chlorination of diphenyl ether (Mailhe and Murat, *loc. cit.*).

2-Nitrodiphenyl sulphide is unaffected by piperidine under conditions sufficing to effect partial scission of 2-nitrodiphenyl ether. Similarly, 2 : 4-dinitro- and 2 : 4 : 6-trinitro-*N*-ethyldiphenylamine do not react with piperidine. *p*-Nitrophenol is unaffected when boiled for some time with piperidine. It is hoped to investigate such cases in greater detail.

EXPERIMENTAL.

Action of Piperidine on 2- and 4-Nitrodiphenyl Ether and 2′-, 3′-, and 4′-Chloro-2-nitrodiphenyl Ether.—These ethers were heated for 30 minutes at 100° with an excess of piperidine. In each case, slight reaction occurred, as was evidenced by the odour of phenol, phenol, *o*-, *m*-, and *p*-chlorophenols, respectively, after acidification. Interaction was, however, insufficiently complete to allow of the isolation of any definite piperidino-derivative from the reddish, oily products.

4-*Bromo*-2 : 4′-*dinitrodiphenyl Ether.*—When 10 g. of 2 : 4-dinitrodiphenyl ether were heated with 12·3 g. of bromine in glacial acetic acid in presence of sodium acetate at 100°, 12·5 g. of the bromodinitro-compound, m. p. 134—136·5°, were obtained. One crystallisation from glacial acetic acid raised the m. p. to 136—137·5°. Raiford and Colbert (*J. Amer. Chem. Soc.*, 1926, 48, 2652) give m. p. 138·5°.

2 : 4-*Dibromo*-2′ : 4′-*dinitrodiphenyl ether* was prepared by heating

a mixture of 10 g. of 2 : 4-dibromophenol, 1·1 g. of potassium hydroxide, and 4 g. of 1-chloro-2 : 4-dinitrobenzene at 100° for 1·5 hours. After being extracted with alkali and with water, the product separated from glacial acetic acid in pale yellow crystals (9·5 g.), m. p. 131° (Found : Br, 38·3. $C_{12}H_6O_5N_2Br_2$ requires Br, 38·3%).

Action of Piperidine on 2 : 4-Dinitro- (I), *4′-Bromo-2 : 4-dinitro-* (II), *2′ : 4′-Dibromo-2 : 4-dinitro-, and 2 : 4 : 2′ : 4′-Tetranitro-diphenyl Ether.*—Each of these ethers gave a yellow to red coloration with cold piperidine, and on warming, a vigorous reaction set in. The resulting solution, on dilution with water, gave almost pure 2 : 4-dinitrophenylpiperidine (Lellmann and Geller, *loc. cit.*). This, after one crystallisation from alcohol, had m. p. 92°. The four aqueous filtrates, when acidified, etc., gave phenol, *p*-bromophenol, 2 : 4-dibromophenol, and 2 : 4-dinitrophenol, respectively.

Action of Piperidine on 5-Chloro-2-nitrodiphenyl Ether.—(1) *Two mols. of piperidine.* To a solution of 2·5 g. (1 mol.) of the ether in 10 c.c. of chloroform were added 2·2 c.c. of piperidine (2·25 mols.) dissolved in 5 c.c. of chloroform. The mixture was boiled for 2 minutes, the chloroform removed by evaporation, and the residual oil left in a vacuum for a week, then washed with light petroleum, and crystallised from alcohol–light petroleum. *5-Piperidino-2-nitrodiphenyl ether* was thus obtained in yellow needles, m. p. 86—86·5° (Found : N, 9·5. $C_{17}H_{18}O_3N_2$ requires N, 9·4%). (2) *Excess of piperidine.* On addition of the chloronitro-ether (2 g.) to 5 c.c. of piperidine and gentle warming, a definite reaction occurred; the solution soon set to a magma of crystals. The whole was heated for ½ hour; a clear reddish-brown solution then resulted. Dilution gave an oil, which, after being washed, was extracted with benzene. The extract was dried over sodium sulphate and evaporated, and the solid residue crystallised from alcohol. The orange crystals obtained melted at 67° and were identical (mixed melting point) with the product of interaction of 2 : 4-dichloro-1-nitrobenzene with piperidine (Le Fèvre and Turner, this vol., 1113).

4-Bromo-4′-nitrodiphenyl Ether.—*p*-Bromophenol, *p*-chloronitrobenzene, and potassium hydroxide, the last dissolved in the minimal quantity of water, were allowed to condense in the usual manner. After extraction and distillation in a vacuum, the *bromonitro-ether* crystallised from alcohol in colourless prisms, m. p. 60°, b. p. 230°/15 mm. (Found : Br, 27·3. $C_{12}H_8O_3NBr$ requires Br, 27·2%).

4-Bromo-4′-aminodiphenyl Ether and 4 : 4′-Dibromodiphenyl Ether.—The preceding nitro-compound, when reduced with water, iron powder, and ferric chloride, gave an 84% yield of the crude amino-compound, which was at once diazotised and converted into the diazo-perbromide. This, when decomposed in hot glacial acetic acid, gave dibromodiphenyl ether, which, after crystallisation from alcohol, melted at 60°. This compound did not depress the m. p. of the product (m. p. 60·5°; b. p. 210°/11 mm.) obtained by direct bromination of diphenyl ether by Hoffmeister's method (*loc. cit.*).

Dinitration of 4 : 4'-*Dibromodiphenyl Ether.*—A solution of the dibromo-compound in 10 parts of nitric acid (*d* 1·5) was heated at 100° for ½ hour and then poured into water. The precipitated solid separated from glacial acetic acid in small needles, m. p. 167° (Found : Br, 38·0. $C_{12}H_6O_5N_2Br_2$ requires Br, 38·3%).

Mononitration of 4 : 4'-*Dibromodiphenyl Ether.*—A solution of 20 g. of dibromodiphenyl ether in glacial acetic acid was treated with one of 8 g. of potassium nitrate in concentrated sulphuric acid. The solution was warmed at 100° for an hour, then cooled, and kept. The crystalline deposit separated from glacial acetic acid in small prisms, m. p. 90—91° (Found : Br, 42·5. $C_{12}H_7O_3NBr_2$ requires Br, 42·9%).

4-*Chloro*-4'-*nitrodiphenyl Ether.*—Condensation, by the usual process, of *p*-chloronitrobenzene, *p*-chlorophenol, and potassium hydroxide gave a product which, after alkali-washing and distillation in a vacuum, was crystallised from alcohol; it then had m. p. 75·5—76° and b. p. 215°/12 mm.

4-*Chloro*-4'-*aminodiphenyl Ether.*—Reduction of the preceding nitro-compound with iron, water, and ferric chloride gave an almost theoretical yield of crude amine. The latter crystallised from alcohol in colourless prisms, m. p. 100° (Found : Cl, 16·0. $C_{12}H_{10}ONCl$ requires Cl, 16·2%).

4 : 4'-*Dichlorodiphenyl Ether.*—The amino-compound was diazotised and submitted to the Sandmeyer reaction; after the usual procedure, the dichloro-compound separated from alcohol in colourless needles, m. p. 30°.

Nitration of 4 : 4'-*Dichlorodiphenyl Ether.*—The dichloro-compound was dissolved in 10 parts of nitric acid (*d* 1·5), and the solution warmed gently for 15 minutes. On cooling, crystals separated. These crystallised from glacial acetic acid in slender, white needles, m. p. 152° (Found : Cl, 21·4. $C_{12}H_6O_5N_2Cl_2$ requires Cl, 21·6%).

The dinitro-compound was dissolved in excess of piperidine, and the solution was boiled for 10 minutes. Dilution and filtration gave a solid, which, after being crystallised from glacial acetic acid, melted at 48° and was identical with 4-chloro-2-nitropiperidinobenzene (Le Fèvre and Turner, *loc. cit.*).

The filtrate from the above solid was acidified, and submitted to steam distillation; 4-chloro-2-nitrophenol then passed over. Its identity was established by comparison with a sample prepared by heating 2 : 5-dichloronitrobenzene with 50% aqueous potassium hydroxide at the b. p. for 2 hours. Both specimens, and a mixture, melted at 87—88°.

Mononitration of 4 : 4′-*Dichlorodiphenyl Ether*.—To a solution of the dichloro-ether in glacial acetic acid was added a solution of 1·25 mols. of potassium nitrate in concentrated sulphuric acid. The mixture was warmed on the water-bath for an hour and diluted, and the precipitate was collected. It crystallised from alcohol in wads of short, white needles, m. p. 75°. Its m. p. was unaffected by admixture with a specimen prepared as follows: *p*-Chlorophenol, 2 : 5-dichloronitrobenzene, and potassium hydroxide were condensed together in the usual manner, and gave a product which, after extraction with alkali, boiled at 215—220°/15 mm. After crystallisation from alcohol, it had m. p. 75°.

Nitration of 4 : 4′-*Dichloro*-2-*nitrodiphenyl Ether*.—A solution of the nitro-compound in 10 parts of fuming nitric acid (*d* 1·5) was warmed for 10 minutes and then diluted. Filtration, followed by crystallisation from glacial acetic acid, gave the dinitro-compound, m. p. 152°, identical (mixed m. p.) with that obtained above from 4 : 4′-dichlorodiphenyl ether.

One of us (R. J. W. Le F.) has pleasure in acknowledging a maintenance grant from the Department of Scientific and Industrial Research, and the receipt of a grant from the Research Fund of the Chemical Society.

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UNIVERSITY OF LONDON.

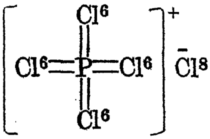
[*Received, March 24th,* 1927.]

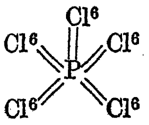
CLXIII.—*The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorus and Antimony.*

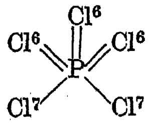
By SAMUEL SUGDEN.

SOME time ago Dr. N. V. Sidgwick suggested to the author that it would be of interest to examine the parachors of substances in which a central atom appears to share electrons with more than four other atoms. Substances of this type have a particular interest from the point of view of the electronic theory of valency, for it is difficult to formulate them satisfactorily without abandoning the octet rule or the conception of the sharing of electrons in pairs.

Three electronic formulæ have been suggested for phosphorus pentachloride. The polar formula (I) (Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 919) is open to many criticisms : phosphorus pentachloride is readily fusible (under pressure) and volatile, its solutions do not conduct electricity, and in general the substance has none of the properties of a salt. For these reasons, Lewis (" Valence and the Structure of Atoms and Molecules," 1923, p. 101) adopts formula (II) and considers that substances of this type are exceptions to the octet rule. On the other hand, Prideaux (*Chem. and Ind.*, 1923, **42**, 672) maintains the rule of eight by discarding the duplet rule for two of the chlorine atoms which are supposed to be bound by sharing one electron each with the phosphorus atom, as shown in formula (III).


−1·6
(I.)


+7·7
(II.)


−24·8
(III.)

For this method of formulation the author is indebted to Dr. J. D. Main Smith. Each bond indicates a shared electron, whilst the superscript figures give the number of unshared electrons.

This conception of a single-electron linkage (which for brevity will be termed a singlet), in which one electron is held in common by two atoms, played an important part in the earlier electronic theories of Stark ("Atomdynamik," Hirzel, Leipzig, 1916) and was suggested by Thomson (*Phil. Mag.*, 1921, **41**, 510) for the hypothetical NCl_5. More recently, Prideaux's formula for phosphorus pentachloride has been applied by Ingold and Ingold (J., 1926, 1315) to explain certain cases of substitution in the aromatic series. As these authors point out, the singlet linkage in this compound is a semipolar single bond, for it consists of half a covalency and half an electrovalency. If a shared electron is counted as half value for each of the atoms which share it (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), there is found to be a positive charge on the phosphorus atom and an effective half negative charge on each of the chlorine atoms held by a singlet. This half charge does not, of course, signify a splitting of the electron, but may be interpreted dynamically on the lines suggested by Højendahl (J., 1924, **125**, 1381) as a statistical average obtained by integrating the field of the electron in the neighbourhood of a particular atom over a time interval which is large compared with the period of revolution in its orbit. From this point of view it is obvious that the effective polarity of a shared electron will only be exactly 0·5 if its orbit lies symmetrically about or between the two atoms which share it; the small variations in polarity discussed by Højendahl on this basis need not be considered here, and, with this reservation, the value 0·5 will be used in calculating polarities.

The most important difference between the point of view expressed by formulæ (II) and (III) is that in (II) the duplet is maintained and the octet rule abandoned, whilst in (III) the octet is completed by violating the rule that electrons are shared only in pairs. It is therefore of interest to inquire what general experimental evidence can be adduced in favour of these two hypotheses. The conception of duplets (Lewis, *loc. cit.*) is based upon (*a*) the occurrence of electrons in pairs at each quantum level throughout the structure of atoms, and (*b*) the presence of an even number of valency electrons in by far the greater number of stable molecules. This, however, can scarcely be regarded as proving the invariable covalency linkage of two electrons. Sufficient "odd" molecules exist to show that the pairing of electrons, although very common, is not necessary for the formation of stable molecules; also pairs of singlet linkages, as in formula (III), may well be present in molecules containing an even number of valency electrons.

On the other hand, the rule of eight can now be supported by a much greater body of experimental evidence. It is an essential feature of Bohr's theory of atomic structure that all the inert gases contain eight electrons of greatest principal quantum number. This conception is retained in the further sub-division into grouplets (Main Smith, "Chemistry and Atomic Structure," Benn, 1924; Stoner, *Phil. Mag.*, 1924, 48, 719), which has now been shown to give a satisfactory explanation of *X*-ray absorption edges and the complex phenomena of multiplet structure in optical spectra. The volume of physical evidence in favour of the Bohr–Main Smith–Stoner scheme of the distribution of extra-nuclear electrons is now so large that it is highly improbable that any further advance in knowledge will necessitate a serious modification of its main features.

The octet rule has also been shown to predict accurately the occurrence and number of semipolar double bonds in a series of compounds of nitrogen, phosphorus, and sulphur (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525) and further striking evidence for the existence of this type of linkage has been obtained by the preparation of three new types of optically active sulphur compounds by Phillips and his collaborators (J., 1925, **127**, 2522; 1926, 2079; this vol., p. 188). In all these cases the existence of the semipolar double bond indicates that the number of electrons associated with the atoms of nitrogen, phosphorus, and sulphur does not exceed eight.

From these considerations, it appears probable that in compounds of the type of phosphorus pentachloride the rule of eight will still be valid and that (III) represents the structure of this compound better than (II). It is evident, however, that the case for the existence of singlet linkages would be very much strengthened if this rather indirect evidence could be supported by observation of an effect due directly to the presence of singlets. Such evidence is now furnished by the effect of singlets upon the parachor.

The Parachor and Singlet Linkages.

It has been shown (Sugden and Wilkins, this vol., p. 139) that the effect of unsaturated linkages upon the parachor is very nearly proportional to the excess of electrons above two in the linkage considered. Some of the values found are in Table I; the constants for ring structures are not recorded, but they lie between those found for the non-polar double and the single bond, and they can be predicted with fair accuracy on the assumption that they are proportional to the degree of unsaturation.

TABLE I.

Linkage.	No. of electrons.	Parachor.
Triple bond	6	46·6
Non-polar double bond	4	23·2
Single bond (duplet)	2	(0·0)
Semipolar double bond	2	−1·6
Singlet	1	−11·6
Semipolar single bond	1	−12·4

The duplet linkage (the chemical single bond) is of necessity neglected when the atomic constants are computed and must therefore be regarded as an arbitrary zero or normal level from which the effect of other linkages is measured. For the double and the triple bond and for ring structures, each electron above two adds 11·6 units to the molecular parachor; it seems probable, therefore, that this scale can be extended downwards and that the singlet linkage containing one electron less than the duplet will lower the parachor by 11·6 units. When a half-polar bond is present, as in phosphorus pentachloride, there must be added to this the effect of half a polar linkage, which, by comparison with the value for a semipolar double bond (duplet + polar bond), will be − 0·8. The total effect for a semipolar single bond should therefore be − 12·4 units. The singlet linkage is not always polar (compare the formula for acetylacetone derivatives, VIII, p. 1179) and when neutral would have a value of − 11·6 units; the difference is, however, less than the usual error of experiment. The two singlets in formula (III) should therefore give a change of − 24·8 in the molecular parachor.

The polar bond in formula (I) should produce an effect of − 1·6 units only. This value is obtained from the observed effect of the semipolar double bond which consists of a covalency plus an electrovalency. Since a covalency = 0, it follows that an electrovalency = − 1·6. Further evidence for this value is given by the parachors of the halogen hydrides recorded in Table II, calculated from the observations of Steele, McIntosh, and Archibald (*Z. physikal. Chem.*, 1906, **55**, 145). The surface-tension determinations of these workers are based upon the data of Ramsay and Shields and have therefore been corrected as indicated in an earlier paper (Sugden, J., 1924, **125**, 33). This correction increases the value of the parachor by about 1%.

TABLE II.

Substance.	[*P*]obs.	Σ[*P*].		Polar bond.
HCl	67·8	71·4		−3·6
HBr	85·4	85·1		+0·3
HI	105·3	108·1		−2·8
			Mean	−2·0

It is evident that these substances give the same structural constant as the semipolar double bond within the limits of experimental error (± 2 units). It is possible, of course, to argue that in the liquid state the halogen acids are not polarised and that the hydrogen atom is linked by a covalency. On this view, however, the structural constant for formula (I) would also be negligibly small, for it appears highly improbable that liquid phosphorus pentachloride is polar whilst liquid hydrogen chloride is not. A fuller discussion of this point will be given in a later paper in which the data for fused salts will be discussed.

The effect of the enhanced valency shell in formula (II) is rather more difficult to predict. The relation set out in Table I appears to be interpreted most simply by assuming that the effect of linkages upon the parachor is determined chiefly by the space required to accommodate the orbits of the shared electrons, and is very nearly a linear function of the number of shared electrons. On this view, the effect of the structure in (II) may be estimated roughly as follows. Since two extra electrons are shared between six atoms, the effect should be one-third of that found when two extra electrons are shared between two atoms in the non-polar double bond, *i.e.*, 23·2/3 or + 7·7 units.

The parachors for the pentachlorides of antimony and phosphorus have now been determined and are recorded in Table III. The column headed Σ[*P*] gives the sum of the atomic constants, and the last column shows the difference between [*P*]obs. and Σ[*P*], thus giving the effect of any special structure present in the mole-

TABLE III.

Substance.	[P]obs.	$\Sigma[P]$.	Structural constant.
Phosphorus pentachloride ...	282·5	309·2	−26·7
Antimony pentachloride	311·8	337·5	−25·7

cule. It will be seen that for both substances the value found for the structural constant is very close to the predicted effect of two singlet linkages, but differs widely from the expected effect of the structures represented by formulæ (I) and (II).

The atomic constant of phosphorus, used in calculating $\Sigma[P]$, has been determined from a number of compounds of this element for which data have already been recorded (Sugden, Reed, and Wilkins, *loc. cit.*). The constant for antimony was obtained from the data shown in Table IV in which $\Sigma[P]$ is the sum of all the atomic and structural constants in the molecule except that for the antimony atom. The mean value, 66·0, can scarcely be in error by more than ± 2 units.

TABLE IV.

Substance.	[P]obs.	$\Sigma[P]$.	Antimony.
Antimony trichloride	227·4	162·9	64·5
Triphenylstibine	637·4	570·0	67·4
		Mean	66·0

It should be mentioned that the anomaly exhibited in Table III cannot be accounted for by association of the liquid pentachlorides. Highly associated liquids, *e.g.*, alcohols, have a parachor which is only a few units below the predicted value and which increases as the temperature rises, but the pentachlorides examined show no signs of association—the parachor is nearly independent of temperature and the molecular weights of these substances in organic solvents are normal.

The difference between [P]obs. and $\Sigma[P]$ is therefore real, and since the additive nature of the parachor has been verified for a large number of substances, the conclusion seems inevitable that in these pentachlorides a type of valency linkage is present which has not been encountered in earlier work. It is submitted that by far the simplest interpretation of this result, which is in harmony with the established effect of well-known types of valency linkage, is the hypothesis that two singlet linkages are present in the molecule.

If this conclusion is accepted, it follows that the existence of singlet linkages can be detected, and their number determined, by means of the parachor. The extension of the electronic theory of valency to include singlet linkages, or more generally odd-electron linkages, can therefore be subjected to a direct experimental test and has no longer a purely speculative basis; it opens up a wide field for future investigation, as will be seen from the following brief account of the more important theoretical consequences.

Applications of the Theory of Odd-electron Linkages.

The formulæ suggested below are based upon the following three rules :

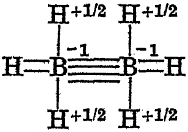
(1) The number of electrons associated with each atom (except hydrogen) does not exceed, and wherever possible is equal to, eight (the octet rule of Lewis).

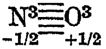
(2) Atoms may share 1, 2, 3, 4, 5, or 6 electrons with another atom.

(3) The polarity of an atom in a compound is calculated by reckoning shared electrons at half their value, as proposed by Lowry (*loc. cit.*). When alternative formulæ are possible, the one showing the smallest development of polarity is the more probable.

Simple Compounds.—The application of the theory of odd-electron linkages to compounds of the type of SF_6, SCl_4, IF_5, ICl_3, OsF_8, etc., is obvious and has already been discussed by Prideaux (*loc. cit.*). Less obvious is the fact that borethane (IV) and nitric oxide (V) can be formulated with complete octets. Thomson's symmetrical formula for benzene (compare Sugden and Wilkins, J., 1925, **127**, 2518) also involves triplet linkages.

(IV.)



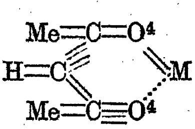


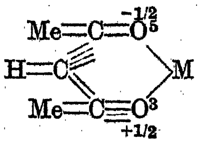
$$\underset{-1/2}{N^3}\equiv\underset{+1/2}{O^3}$$

(V.)

Chelate Linkages.—Singlet linkages give a simple explanation of the hypothetical residual valency bonds assumed to exist in many chelate groups. The oxalyl radical and ethylenediamine can, of course, be linked by two duplets, but in acetylacetone derivatives the metal is supposed to be attached to the second oxygen atom by a residual valency often indicated by a dotted line. This is shown in (VI) in which M represents one equivalent of a metal. The metal can, however, be attached to both oxygen atoms by singlets as in (VII); this formula contains polar oxygen atoms which can be neutralised by replacing the two double bonds by four triplets as in (VIII), in which all the atoms are neutral.

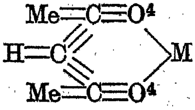
(VI.)

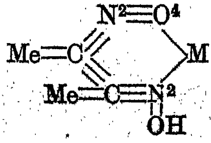




(VII.)

(VIII.)





(IX.)

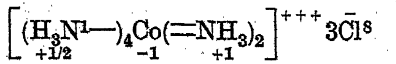
Formula (IX) represents in similar fashion the structure of derivatives of dimethylglyoxime, and gives a neutral molecule in which all the atoms, except hydrogen, have complete octets. It will be seen that the metal is co-ordinated with oxygen and nitrogen; if it is co-ordinated with the two oxygen atoms it incurs unlikely polarities.

Co-ordination Compounds.—In the older form of the electron theory of valency the existence of co-ordination numbers higher than 4 seemed to necessitate the abandonment of the octet rule. If singlet linkages are used, co-ordination numbers of 5, 6, 7, and 8 can readily be accounted for by the presence of 2, 4, 6, and 8 singlet linkages, respectively.

The cobaltammines and similar compounds can easily be formulated by building up an octet in the valency shell of the ion of the metal. This involves the assumption, first put forward by Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762) and elaborated by Bury (*ibid.*, 1921, **43**, 1602), that the electronic structure of the transition elements is not uniquely determined. This suggestion has been verified by recent work on optical spectra, and the table of electronic configurations compiled by McLennan, McLay, and Smith (*Proc. Roy. Soc.*, 1926, **112**, 76) contains a number of examples of alternative structures which give rise to different groups of lines in the spectra of one element.

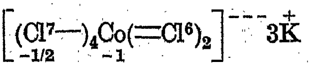
The structures of hexamminocobaltic chloride and potassium hexachlorocobaltiate are represented on this view by (X) and (XI). The polarities of the atoms are indicated in the formulæ, and it will be seen that in both cases the central cobalt atom has a net charge of − 1, since its original charge of + 3 is more than neutralised by sharing 8 electrons with the co-ordinated groups. The net charge of the complex ion as a whole is predicted correctly by summing the polarity of each group as indicated in the formulæ.

The corresponding derivatives of iron, chromium, and nickel can readily be formulated in a similar manner. The formula for potassium ferricyanide is, *mutatis mutandis*, similar to (XI). The replacement of the ferric ion by the ferrous ion merely alters the charge on the complex ion from − 3 to − 4 in potassium ferrocyanide. In all these formulæ a definite structure in harmony with the octet rule is assigned to the complex within Werner's square brackets



$$\left[(\underset{+1/2}{H_3N^1}—)_4\underset{-1}{Co}(=\underset{+1}{NH_3})_2\right]^{+++}3\overset{-}{Cl}{}^8$$

(X.)



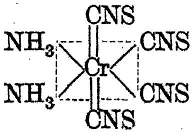
$$\left[(\underset{-1/2}{Cl^7}—)_4\underset{-1}{Co}(=Cl^6)_2\right]^{---}3\overset{+}{K}$$

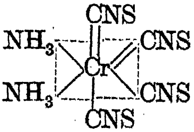
(XI.)

by substituting singlet linkages for the less clearly-defined " residual affinities." The recent work of Burgess and Lowry (J., 1924, **125**, 2081), Mills and Gotts (J., 1926, 3121), and Mann and Pope (*ibid.*, p. 2675) shows clearly that residual affinities are sufficiently well-defined entities to be capable of bringing about molecular asymmetry, and in all the compounds studied by these investigators singlet linkages can be employed to give a concrete picture of the bonds which are presumed to be responsible for the development of optical activity.

It would appear at first that formula (X) would give too many isomerides for co-ordination compounds containing two or more different radicals within the complex. The restrictions of the polarity rule (p. 1179), which means in this case that the duplet linkages are, wherever possible, associated with negative groups, reduce the number of possible isomerides in most cases to that which would be expected on the usual theory of a symmetrical octahedral structure. One interesting difference is found for substances of the type of Reinecke's salt, $NH_4[Cr(CNS)_4(NH_3)_2]$, which on the singlet theory might exist in two forms, (XII) and (XIII); the second of these, in which the duplets are *cis*, should be resolvable.

(XII.)



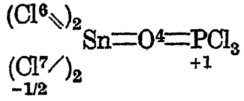


(XIII.)

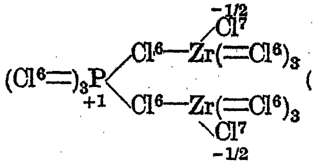
Since, however, a duplet linkage is much more bulky than a singlet, it appears probable that the normal form has the *trans*-structure (XII).

Molecular Compounds.—A large number of additive compounds, formed by the higher halides of Groups IV, V, and VI, are not readily formulated on Werner's co-ordination theory; some of these possess an extraordinary stability, *e.g.*, $SnCl_4,POCl_3$, b. p. 180°; $2ZrCl_4,PCl_5$, b. p. 416°; $2ZrCl_4,POCl_3$, b. p. 363°. All these compounds can be formulated by using singlet linkages. In general, the formulæ are obtained by supposing that two of the halogen atoms in one molecule, which were originally linked by duplets, become linked by singlets; the central atom is then sharing only 6 electrons and can link with a lone pair of electrons in the second compound. Formula (XIV) gives such a structure for $SnCl_4,POCl_3$; similar formulæ account for the well-known series of additive compounds of stannic chloride with ketones which have the composition $SnCl_4,2R_1R_2CO$. In the corresponding series of compounds with antimony pentachloride, the compounds so far described have the compositions $SbCl_5,R_1R_2CO$ or $2SbCl_5,3R_1R_2CO$; these are exactly the compounds to be expected if the linkage between the molecules is made possible by the conversion of halogens linked by duplets into halogens linked by singlets. The very stable compound $2ZrCl_4,PCl_5$ appears to be of a rather different type in which each

(XIV.)



$$\begin{matrix}(Cl^{6}\searrow)_2 \\ \underset{-1/2}{(Cl^{7}\swarrow)_2}\end{matrix}Sn{=}O^{4}{=}\underset{+1}{PCl_3}$$



(XV.)

of the chlorine atoms originally linked by singlets shares an electron with a zirconium atom (XV). A similar structure can be written for the corresponding compound with phosphorus oxychloride.

Finally, the singlet linkage gives a concrete picture of the vague term " residual affinity " used to explain so many chemical changes, *e.g.*, the Wagner–Meerwein transformation, the *trans* Beckmann change, etc.; in many of the theories of these reactions, in which a residual affinity becomes a complete covalency after a series of changes, the use of singlet linkages gives a clearer picture of the mechanism of the reaction. Another interesting aspect of the singlet, when it forms a semipolar single bond, is that it is a definite half-way stage between a covalency and a polar valency.

Sufficient has been said to show that the theory of odd-electron linkages here put forward is capable of simplifying and correlating a large body of chemical knowledge. Furthermore, it leads to conclusions (*e.g.*, the magnitude of the parachor) which can be subjected to an experimental test, and therefore fulfils all the requirements of a sound working hypothesis. In succeeding papers of this series it is hoped to apply this and other tests to a number of the substances formulated above; many of them are fusible without decomposition and can therefore be dealt with by the experimental methods described in this and other papers on the parachor.

EXPERIMENTAL.

In the course of this investigation measurements have been made of the surface tension and density of phosphorus pentachloride, antimony trichloride, and antimony pentachloride. From these, the parachors were calculated by the relation $P = \gamma^{1/4}/(D - d)$, where γ is the surface tension, and D and d are the densities of the liquid and saturated vapour, respectively.

Phosphorus pentachloride was purified by sublimation and stored in sealed tubes. It melted in a closed tube at 163—164° (corr.), which is much higher than the value, *viz.*, 148°, given by Casselmann (*Annalen*, 1852, **83**, 247). A small infusible residue remained when a quantity of the substance was melted; this appeared to be insoluble in the liquid and since its amount was small it is believed not to have any serious effect upon the surface-tension or density measurements.

Since the pentachloride has a large vapour pressure at its melting point, all the measurements had to be carried out in sealed vessels. The density of the liquid was therefore determined by the method of flotation. Small glass floats about 5 × 1 × 1 mm. were prepared and the temperature was determined (to the nearest 0·5°) at which they were in equilibrium with a suitable mixture of bromoform and benzene. The density of the liquid at this temperature was then determined by means of a pyknometer.

Each float was placed in a marked piece of quill tubing sealed at one end. One of the storage tubes was then broken and the open end of the quill tube forced into the mass of pentachloride until a sufficient quantity of the substance had been picked up; the pentachloride was rapidly tapped down to the closed end, and the tube sealed off. In this way exposure to the atmosphere for more than a few seconds was avoided and only a negligible quantity of moisture could have been absorbed.

Tubes filled in this manner were supported in a glycerol-bath provided with a thermometer and stirrer, and the temperatures of flotation were determined. Molten phosphorus pentachloride proved to be a mobile liquid and no difficulty was experienced in fixing the flotation temperatures to within ± 0·5°. The following results were obtained.

Float	1	5	6
Density	1·482	1·520	1·559
Flotation temp. (corr.)	218°	200·5°	181°

$$\text{whence } D = 1{\cdot}624 - 0{\cdot}00208\,(t - 150).$$

A rough determination of the vapour pressure (dissociation pressure) was next made to ascertain the order of magnitude of the pressure within the tubes. This proved to be unexpectedly small, so that the density of the vapour could be calculated with sufficient accuracy from the vapour-pressure observations.

A quantity of the pentachloride was confined in a bulb of about 5 c.c. capacity connected to a capillary tube bent at right angles to give a long capillary limb. An index of mercury separated the gas in the bulb from a fixed quantity of air in the long limb of the apparatus; the distant end of the capillary tube was sealed whilst the whole apparatus was at a known temperature and at atmospheric pressure. The bulb was then heated in a glycerol-bath, and the volume of the air in the long limb measured by means of a millimetre scale. From this volume, the total pressure in the apparatus was calculated; by subtracting the pressure of the air present initially in the bulb, the vapour pressure (in atm.) of the pentachloride was obtained.

t (corr.).	Reading.	p_{total}.	p_{air}.	p_{PCl_5}.
13°	24·3	1·00	1·00	—
142·5	14·1	1·72	1·45	0·27
163	11·1	2·41	1·52	0·67
182	8·1	3·00	1·59	1·41
195·5	6·6	3·68	1·64	2·03

These figures can only be regarded as a rough approximation, but they indicate that below 200° no great pressure is developed. From the results, the density of the vapour at the three temperatures used for the measurement of the surface tension was calculated as follows. If the gas laws can be assumed to hold for the vapour, the density is given by $d = Mp/RT$, where M is the molecular weight and p the pressure. For phosphorus pentachloride a correction must be applied for the degree of dissociation, α, so that the formula becomes, putting $M = 208{\cdot}3$ and expressing R in c.c.-atm., $d = 2{\cdot}54\ p/(1 - \alpha)T$. The pressure p was interpolated from the figures given above, whilst the dissociation constant K was obtained from the observations of Cahours (*Annalen*, 1867, **141**, 42). Incidentally, it may be noted that, since the degree of dissociation in the vapour is less than 50%, the dissociation of the liquid must be very small. The calculation of d is set out below; as the values found are small compared with the liquid density, they need not be known with great accuracy, since it is the quantity $(D - d)$ which is used in calculating the parachor.

t (corr.).	p (atm.).	K.	α.	d.	D.	$D - d$.
169·5°	0·78	0·175	0·43	0·0031	1·583	1·580
181	1·02	0·205	0·41	0·0041	1·560	1·556
192	1·81	0·255	0·35	0·0073	1·537	1·530

The surface tension was measured by the method of capillary rise, the apparatus and microscope fittings already described by the author (J., 1921, **119**, 1483) being used. Apparatus 3 was employed for which $r_1 = 0{\cdot}005495$ cm. and $r_2 = 0{\cdot}1310$ cm. The method of calculating a^2 from the capillary rise, H, was described in the above paper. The following results were obtained :

t (corr.).	H (mm.).	a^2 (mm.^{2}).	$D-d$ (g./c.c.).	γ (dynes/cm.).	Parachor.
169·5°	3·027	2·690	1·580	20·9	281·8
181	2·918	2·592	1·556	19·8	282·5
192	2·815	2·496	1·530	18·7	283·1
				Mean	282·5

[With ADOLPH FREIMAN.]

The surface tensions of antimony tri- and penta-chlorides were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The tables are set out in the manner described in earlier papers of this series. The bubbler used was No. 16a, and had the following constants : $r_2 = 0{\cdot}179$ cm., $A = 0{\cdot}008271$.

Antimony trichloride, $M = 228{\cdot}2$, was purified by distillation and had b. p. 219° (corr.). Densities determined : $D_{4°}^{95{\cdot}5°}$ 2·632, $D_{4°}^{123{\cdot}5°}$ 2·565, $D_{4°}^{149{\cdot}5°}$ 2·510; whence $D_{4°}^{t°} = 2{\cdot}844 - 0{\cdot}00224t$. These densities are in good agreement with those found by Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1).

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
16a	109·5°	5067	2·599	1·0621	44·51	226·7
,,	127·5	4748	2·558	1·0653	41·84	226·9
,,	148·5	4462	2·511	1·0682	39·43	227·6
,,	166·5	4219	2·471	1·0710	37·38	228·3
						Mean 227·4

Antimony pentachloride, $M = 298{\cdot}1$, was distilled under diminished pressure; the fraction used boiled at 85° (corr.)/55 mm. Owing to the hygroscopic nature of this substance the densities were measured by using a sealed dilatometer. Densities determined : $D_{4°}^{11{\cdot}5°}$ 2·370, $D_{4°}^{16°}$ 2·358, $D_{4°}^{36°}$ 2·319, $D_{4°}^{52°}$ 2·289, $D_{4°}^{78°}$ 2·231; whence $D_{4°}^{t°} = 2{\cdot}392 - 0{\cdot}00204t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
16a	15·5	4130	2·360	1·0692	36·53	311·5
,,	36	3938	2·318	1·0713	34·90	312·5
,,	56	3605	2·278	1·0765	32·11	311·4
,,	68	3447	2·253	1·0792	30·78	311·6
						Mean 311·8

Triphenylstibine, $M = 353{\cdot}0$. The following data are taken from the work of Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 700). Since these investigators used Ramsay and Shields's value for benzene in standardising their apparatus, the surface tensions are corrected by multiplying by 1·0335 (Sugden, J., 1924, **125**, 34).

t.	γ.	γ (corr.).	*D*.	Parachor.
35·1	41·63	43·01	1·4200	636·6
47·0	40·58	41·93	1·4105	637·0
63·1	39·08	40·38	1·3952	637·7
77·3	37·60	38·85	1·3820	637·9
91·2	36·12	37·32	1·3683	637·7
103·0	34·92	36·08	1·3568	637·7
				Mean 637·4

Summary.

(1) The parachors of phosphorus and antimony pentachlorides have been determined and are 26 units below the sum of the atomic constants.

(2) Three formulæ for the structure of these substances from the standpoint of electronic valency theory have been discussed, and

the effect of each upon the parachor has been deduced by the aid of the relation between the parachor and the number of electrons in a linkage.

(3) The formula of Prideaux, in which two singlet linkages are present, is considered to give the best and simplest explanation of the observed anomaly. The parachor can therefore be used to detect the presence of such linkages, since each singlet linkage contributes — 12·4 units to this molecular constant.

(4) The electronic theory has been extended to include linkages composed of odd numbers of shared electrons. The modified theory has been applied to deduce formulæ for the higher halides of Groups V, VI, VII, and VIII, for borethane, nitric oxide, chelate groups, co-ordination compounds, and for a number of "molecular compounds."

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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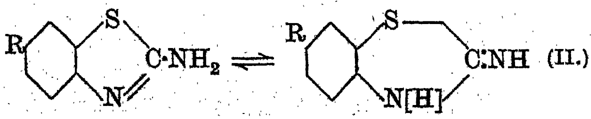
University of London, E.C. 4. [*Received, March 9th, 1927.*]

CLXIV.—*Aminobenzthiazoles. Part VIII. The Effect of Polar Substituents on the Formation and Stability of Nuclear-substituted 1-Aminobenzthiazole Bromides.*

By George Malcolm Dyson, Robert Fergus Hunter, and Richard William Morris.

It appeared probable that valuable evidence for the view that the bromine atoms in the benzthiazole dibromides are held to the nuclear nitrogen atom by means of single electrons (compare Ingold and Ingold, J., 1926, 1385) might be obtained by a study of the effect of different polar substituents on the formation and stability of these compounds. The examination of the bromides of the 5-substituted 1-aminobenzthiazoles (I ⇌ II) was therefore undertaken.

(I.)



(II.)

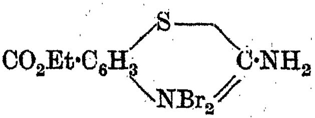
In accordance with the suggested electronic constitutions of these bromo-addition compounds, it was found that negative groups, such as the cyano- and the carbethoxy-group ($R = CN$, CO_2Et, etc.), tended to stabilise the NBr_2 complex in the bromides, whilst positive groups, such as the ethoxy- and the methoxy-group ($R = OEt$, OMe, etc.), had the reverse effect. The stability of the bromides could not be investigated quantitatively, but atmospheric decomposition of the compounds indicated that the effects of the substituents conform to " general polarity," the series being $CN,CO_2Et > Br,Cl > OEt,OMe$ in order of decreasing stability of the bromide. This series is similar to that recorded by Rule and Paterson (J., 1924, **125**, 2155), and by Rule and Smith (J., 1925, **127**, 2188) denoting the relative influence of groups on acidic strengths of aliphatic acids and on velocity of reaction and molecular inductive capacity.

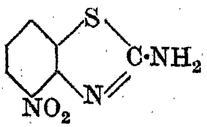
The 5-substituted 1-aminobenzthiazole bromides were obtained by bromination of the corresponding *p*-substituted phenylthiocarbamides in chloroform (Hunter, J., 1925, **127**, 2023, and later papers). These reacted much more slowly than phenylthiocarbamide and its homologues (J., 1926, 1385), resembling in this respect the *s*-*p*-bromophenylalkylthiocarbamides (Hunter and Soyka, J., 1926, 2958), owing possibly to the greater stability of the intermediate ·CBr·SBr compound (Hugershoff, *Ber.*, 1903, **36**, 3121; Hunter and Soyka, *loc. cit.*).

Under the usual conditions of bromination, *p*-cyanophenylthiocarbamide yielded a *tetrabromide* of 1-amino-5-cyanobenzthiazole, which on reduction gave the 5-cyano-base ($I \rightleftharpoons II$; $R = CN$). 1-*Amino*-5-*cyanobenzthiazole*, however, on bromination in chloroform, gave a well-defined *hexabromide*, from which four labile bromine atoms were readily removed by ammonia (compare Macbeth and Hirst, J., 1922, **121**, 904; Macbeth, *ibid.*, p. 1116, and later papers).

Bromination of *p*-carbethoxyphenylthiocarbamide produced a *dibromide* (III) of 1-amino-5-carbethoxybenzthiazole, whereas bromination of 1-amino-5-carbethoxybenzthiazole itself ($I \rightleftharpoons II$; $R = CO_2Et$) gave a *tribromide*, which is doubtless analogous to the tribromides of the 3-thiol-5-keto-2 : 4-dialkyltetrahydro-1 : 2 : 4-thiodiazoles (Freund and Asbrand, *Annalen*, 1895, **285**, 166; Freund and Bachrach, *ibid.*, p. 184).

(III.)





(IV.)

p-Chlorophenylthiocarbamide resembled *p*-carbethoxyphenylthiocarbamide in giving a *dibromide* (of 5-chloro-1-aminobenzthiazole; formula as III), but bromination in chloroform of 5-chloro-1-aminobenzthiazole gave rise to a *hexabromide* similar to that obtained from 1-amino-5-cyanobenzthiazole. Acetylation of the amino-group in 5-chloro-1-aminobenzthiazole, however, somewhat decreased the reactivity of the heterocyclic nucleus, for 5-*chloro*-1-*acetamidobenzthiazole* yielded a *tetrabromide* on bromination under the usual conditions. Bromination of *p*-bromophenylthiocarbamide had previously been observed to give rise to a dibromide of 5-bromo-1-aminobenzthiazole (J., 1926, 1397); by using a higher concentration of bromine, a *tetrabromide*, analogous to the tetrabromide of 1-amino-5-cyanobenzthiazole, has now been isolated.

p-Ethoxyphenylthiocarbamide yielded, on bromination, a *pentabromide* of 1-amino-5-ethoxybenzthiazole, which is probably the hydrobromide of the tetrabromo-addition compound; whereas *p*-methoxyphenylthiocarbamide, under similar conditions, gave rise to a *dibromide* of 1-amino-5-methoxybenzthiazole (formula as III).

1-Amino-5-methylbenzthiazole (I $\rightleftharpoons$ II; R = Me), on bromination, gave an unstable *tetrabromide*, which lost bromine on exposure to air, giving a more stable *tribromide*.

Several unsuccessful attempts were made to prepare 5-dimethylamino-1-aminobenzthiazole (I $\rightleftharpoons$ II; R = NMe_2) by bromination of *p*-dimethylaminophenylthiocarbamide. The formation of a thiazole ring on a benzene nucleus is clearly a case of ortho-substitution and therefore must depend on the *o* : *p*-directive influence of the nitrogen atom which becomes the nuclear nitrogen atom of the dicyclic system. The dimethylamino-group in *p*-dimethylaminophenylthiocarbamide is considerably more basic than the amino-group, and the tendency is, therefore, towards *o* : *p*-substitution with respect to the dimethylamino-group, that is, towards heterocyclic ring formation in the meta-position to the thiocarbamide complex. Such formation is doubtless impossible (compare Perkin and Titley, J., 1922, **121**, 1562; Titley, J., 1926, 508), and benzthiazole ring formation in this case is therefore inhibited.

p-Acetylphenylthiocarbamide behaved anomalously on bromination, yielding a bromo-addition compound which, on reduction with sulphurous acid, gave a complex substance free from sulphur, the exact nature of which has not yet been ascertained.

In view of the low reactivity of 5-nitro-1-phenylbenzthiazole towards bromine (Hunter, J., 1926, 538), the effect of the nitro-group on the unsaturation of the heterocyclic nucleus in 3-*nitro*-1-*aminobenzthiazole* (IV) was also examined. Under the usual conditions of bromination, *o*-nitrophenylthiocarbamide yielded what appeared to be a mixture of a tetrabromide and a tribromide of 3-nitro-1-aminobenzthiazole; on reduction in the usual way, this mixture yielded the base (IV). All attempts to brominate this nitroaminobenzthiazole led only to uncrystallisable bromides, which were not investigated.

EXPERIMENTAL.

The arylthiocarbimides required for this work were obtained by adding a solution of the corresponding nuclear-substituted aniline (1 mol.) in chloroform to a well-stirred suspension of thiocarbonyl chloride (1·3 mols.) in water, and isolating the product in the usual way (Dyson and Hunter, *J. Soc. Chem. Ind.*, 1926, **45**, 83T). The arylthiocarbimides were converted into the corresponding thiocarbamides by treatment with alcoholic ammonia (*loc. cit.*) and were usually recrystallised from alcohol.

Bromination.—The thiocarbamide or the benzthiazole was dissolved in chloroform and treated slowly with a solution of bromine in the same solvent. The benzthiazole bromide separated, in some cases at once, in others after the mixture had been heated under reflux, hydrogen bromide being evolved.

1-*Amino-5-cyanobenzthiazole tetrabromide* (prepared from *p*-cyanophenylthiocarbamide, 1 g.; chloroform, 15 c.c.; bromine, 1 c.c.; time of refluxing, 10—15 minutes) separated as a reddish-brown, crystalline mass, which was collected on porous earthenware and dried in a vacuum over potassium hydroxide. On heating, it became yellow at 60—70°, colourless at about 150°, and melted to a black, viscous liquid at 236° (Found: Br, 64·0. $C_8H_5N_3Br_4S$ requires Br, 64·6%). The compound lost bromine slowly on exposure to moist air, becoming colourless after some days. It liberated iodine from dilute hydriodic acid (Hunter and Soyka, J., 1926, 2962).

1-*Amino-5-cyanobenzthiazole.*—The tetrabromide was suspended in sulphurous acid and treated with sulphur dioxide, and the colourless solution was filtered and treated with ammonia (*d* 0·880); the *base* then separated in white flakes. It crystallised from 50% alcohol in tufts of silky needles, m. p. 196° (Found: S, 18·3. $C_8H_5N_3S$ requires S, 18·3%). This compound was hydrolysed only with difficulty by acids and was usually recovered unchanged after treatment with hydrochloric acid under the usual conditions, this behaviour recalling the similiar properties of 5-cyano-1-phenylbenzthiazole (Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826).

1-*Amino-5-cyanobenzthiazole hexabromide* (prepared from the aminocyanobenzthiazole, 0·3 g.; chloroform, 10 c.c.; bromine, 0·3 c.c.; time of refluxing, 1 minute) separated in golden-brown plates, which, after being dried in a vacuum, gradually lightened in colour on heating and charred at about 290° (Found: Br, 74·0. $C_8H_5N_3Br_6S$ requires Br, 73·2%). This compound had the usual properties and was relatively stable to air. On treatment with ammonia (*d* 0·880) it lost 2 mols. of bromine [Found : Br (labile), 48·4. $C_8H_5N_3Br_2S(Br_4)$ requires Br (labile), 48·9%].

1-*Amino-5-carbethoxybenzthiazole dibromide* (prepared from *p*-carbethoxyphenylthiocarbamide, 1 g.; chloroform, 20 c.c.; bromine, 1 c.c.; mixture refluxed) separated in small, red crystals which melted at 125° (decomp.) after being dried in a vacuum (Found : Br, 42·0. $C_{10}H_{10}O_2N_2Br_2S$ requires Br, 41·8%). The compound had the usual properties, but was relatively stable to air.

On one occasion, the bromination of *p*-carbethoxyphenylthiocarbamide gave rise to a red *tribromide*, m. p. 152° (decomp.) [Found : Br, 53·0. $(C_{10}H_{10}O_2N_2Br_3S)_2$ requires Br, 52·0%].

1-*Amino-5-carbethoxybenzthiazole*.—Either of the preceding bromides was suspended in sulphurous acid and treated with sulphur dioxide until the product was colourless when crushed. The product was then treated with ammonia (*d* 0·880), washed, dried, crystallised from alcohol, and recrystallised from alcohol–ethyl acetate (1 : 1); small, soft, glistening prisms, m. p. 242° (Found : S, 14·0. $C_{10}H_{10}O_2N_2S$ requires S, 14·4%), were thus obtained. On hydrolysis with hydrochloric acid, and extraction with ether, small crystals of 1-*amino-5-carboxybenzthiazole* were obtained, which did not melt on heating.

1-*Amino-5-carbethoxybenzthiazole tribromide* (prepared from the aminocarbethoxybenzthiazole, 0·2 g.; chloroform; bromine, 0·2 c.c.) separated as a red, crystalline mass. The dried substance turned yellow at 150—160°, became colourless on further heating, and melted at 247° (decomp.) [Found : Br, 51·7. $(C_{10}H_{10}O_2N_2Br_3S)_2$ requires Br, 51·9%]. This compound was relatively stable to air, and the labile bromine removed by ammonia (*d* 0·880) corresponded to 24%.

5-*Chloro*-1-*aminobenzthiazole dibromide* was prepared from *p*-chlorophenylthiocarbamide (1·5 g.) as a red, crystalline mass. After being dried, it became colourless at 135° and charred at 215° (Found : Br, 46·0. $C_7H_5N_2ClBr_2S$ requires Br, 46·5%). It had the usual properties and gradually lost bromine on exposure to air, becoming orange, yellow, and finally colourless.

5-*Chloro*-1-*aminobenzthiazole* was precipitated from the solution obtained from the reduction of the dibromide with sulphurous acid, by ammonia, in lustrous plates, m. p. 198°. On recrystallisation from 60% alcohol, it formed aggregates of small, glistening needles, m. p. 199° (Found : Cl, 19·0. $C_7H_5N_2ClS$ requires Cl, 19·2%). The *acetyl* derivative was obtained by boiling a solution of the base in acetic anhydride for a few minutes and pouring it into alcohol. It crystallised from alcohol–ethyl acetate (2 : 1) in small prisms, m. p. 225° (Found : Cl, 13·8. $C_9H_7ON_2ClS$ requires Cl, 15·7%).

5-*Chloro*-1-*aminobenzthiazole hexabromide* was obtained, by bromination of the base in chloroform with excess of bromine, in glistening, golden plates, which were unmelted at 270° (Found: Br, 73·0. $C_7H_5N_2ClBr_6S$ requires Br, 72·3%).

5-*Chloro*-1-*acetamidobenzthiazole tetrabromide* was obtained from 5-chloro-1-acetamidobenzthiazole in orange-yellow crystals, m. p. 215° (after drying) (Found: Br, 57·5. $C_9H_7ON_2ClBr_4S$ requires Br, 58·5%). It was relatively stable to moist air.

5-*Bromo*-1-*aminobenzthiazole tetrabromide*, prepared from *p*-bromophenylthiocarbamide by the method used in the case of 1-amino-5-cyanobenzthiazole tetrabromide, melted at 82—83° with effervescence, giving a yellow solid which became colourless at 170° and melted at 260—262° (decomp.; softening at 258°) (Found: Br, 73·0. $C_7H_5N_2Br_5S$ requires Br, 72·9%). On reduction with sulphurous acid, the tetrabromide yielded 5-bromo-1-aminobenzthiazole, m. p. 211° (Hunter, J., 1926, 1397).

1-*Amino*-5-*ethoxybenzthiazole tetrabromide hydrobromide*, prepared from 1 g. of *p*-ethoxyphenylthiocarbamide, separated in orange-coloured crystals. After being dried in a vacuum, it became colourless at 120—125° and charred at 200° (Found: Br, 67·8. $C_9H_{10}ON_2Br_4S,HBr$ requires Br, 67·3%).

1-*Amino*-5-*ethoxybenzthiazole*.—The preceding hydrobromide was dissolved in a large volume of sulphurous acid (saturated with sulphur dioxide at 15°), and the *base* precipitated with ammonia. After recrystallisation from alcohol–benzene (1 : 2) and from 50% alcohol, it was obtained in small, lustrous prisms, m. p. 174° (Found: S, 16·0. $C_9H_{10}ON_2S$ requires S, 16·5%).

1-*Amino*-5-*methoxybenzthiazole dibromide* (prepared from *p*-methoxyphenylthiocarbamide, 1 g.; chloroform, 20 c.c.; bromine, 1 c.c.) separated in dark brown granules. After drying in a vacuum, it became orange at 70—80°, colourless at 170°, and charred at 240° (Found: Br, 47·9. $C_8H_8ON_2Br_2S$ requires Br, 47·0%). It had the usual properties, but was very unstable and rapidly lost bromine on exposure to the atmosphere.

1-*Amino*-5-*methoxybenzthiazole* was obtained as in the case of the ethoxy-base, and crystallised from 50% alcohol in small, soft plates, m. p. 147° (Found: S, 17·5. $C_8H_8ON_2S$ requires S, 17·7%).

Bromination. The base (0·2 g.) was brominated in chloroform. A black, tarry mass was obtained which, on exposure to air for some days, yielded a violet solid. On heating, this substance became yellow, white and purple in turn and then melted at 220—225° (decomp.) (Found: Br, 48·1%).

1-*Amino*-5-*methylbenzthiazole Tetrabromide*.—One g. of 1-amino-5-methylbenzthiazole (m. p. 140°; Hunter, J., 1926, 1399) was dissolved in 10 c.c. of chloroform and treated with bromine (1 c.c.), a reddish-brown tar (which rapidly solidified) being precipitated. The filtered solution deposited the *tetrabromide* in chocolate-brown plates with a golden lustre. After drying in a vacuum, the tetrabromide lightened in colour at about 180—190°, but was unmelted at 275° (Found : Br, 66·1. $C_8H_8N_2Br_4S$ requires Br, 66·1%). The compound had the usual properties and liberated iodine from a solution of potassium iodide in pure acetic acid. On exposure to air, it lost bromine, leaving a brown, granular, microcrystalline *tribromide*, m. p. 295° (decomp.) [Found : Br, 58·0. $(C_8H_8N_2Br_3S)_2$ requires Br, 59·4%]. This substance was relatively stable to air.

Bromination of p-*Acetylphenylthiocarbamide.*—One g. of *p*-acetylphenylthiocarbamide in chloroform (20 c.c.) was brominated in the usual way; hydrogen bromide was evolved and a bromo-addition compound separated as a bright yellow, crystalline solid, m. p. 137—140° (decomp.). On reduction with sulphurous acid, this yielded a pale yellow, insoluble solid which did not melt below 300°. This substance was free from sulphur, but contained bromine (Found : Br, 20·6%).

3-*Nitro*-1-*aminobenzthiazole.*—One g. of *o*-nitrophenylthiocarbamide was brominated in the usual way, and the mixture refluxed; hydrogen bromide was slowly evolved. The bromo-addition compound formed glistening, orange-brown crystals, m. p. 288° (decomp.), whose composition corresponded most closely with that of a tribromide [Found: Br, 57·2. $(C_7H_5O_2N_3Br_3S)_2$ requires Br, 55·1. $C_7H_5O_2N_3Br_4S$ requires Br, 62·1%]. On reduction with sulphurous acid, the nitroaminobenzthiazole formed a yellow solid, which crystallised from alcohol–ethyl acetate in small, yellow plates which charred at 232° (Found : S, 15·9. $C_7H_5O_2N_3S$ requires S, 16·4%). Attempts to brominate this base led only to uncrystallisable bromides.

Bromination of *o*-bromophenylthiocarbamide in chloroform gave rise to a *tribromide* of 3-bromo-1-aminobenzthiazole which crystallised in glistening, orange plates, m. p. 155° (decomp.; charring at 285—290°) [Found : Br, 69·1. $(C_7H_5N_2Br_4S)_2$ requires Br, 68·2%].

In conclusion, the authors desire to express their gratitude to Professors J. F. Thorpe and C. K. Ingold for their interest in this work, and one of them (R. F. H.) is indebted to the Ramsay Memorial Fellowship Trust for a Fellowship awarded to him and also to the Trustees of the Dixon Fund of the University of London for a grant which has helped to defray the cost of some of the materials.

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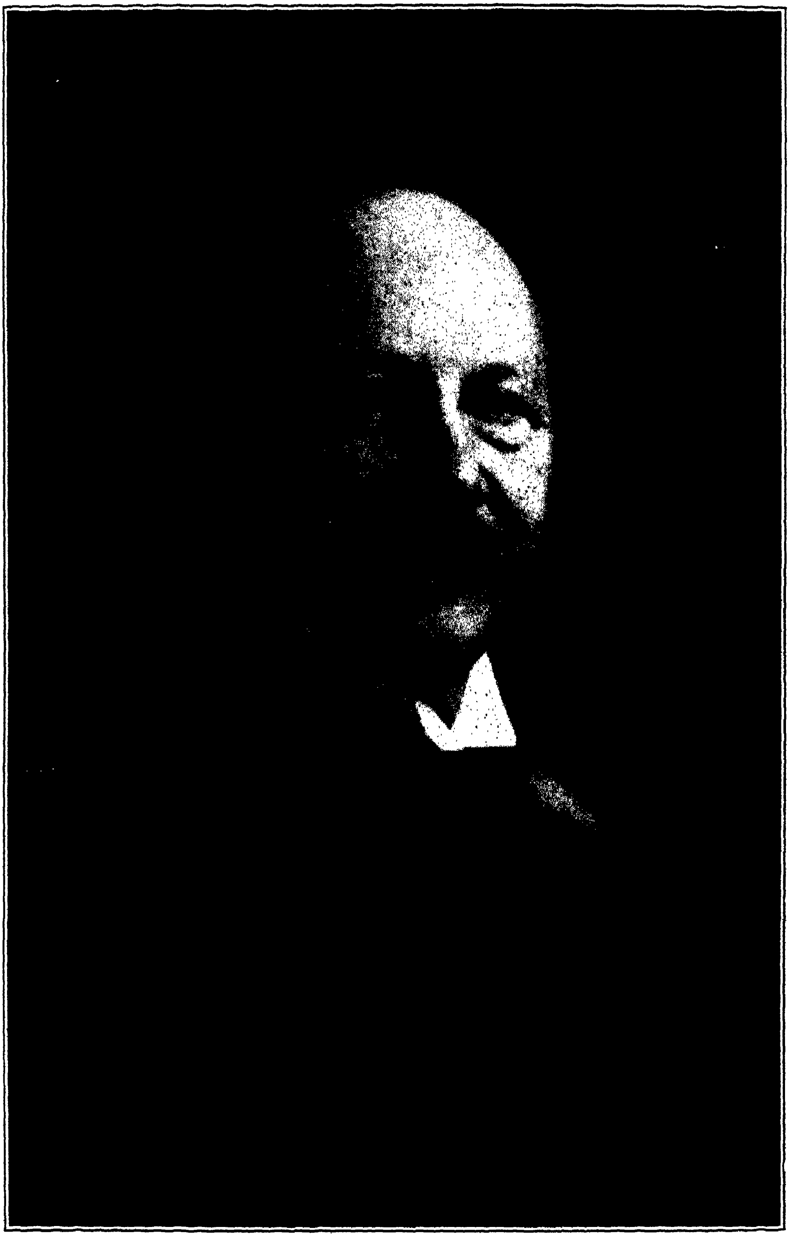
[*Received, December 29th*, 1926.]



HEIKE KAMERLINGH ONNES.

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Kamerlingh Onnes Memorial Lecture.

DELIVERED ON FEBRUARY 10TH, 1927.

By ERNST COHEN, Hon. D.Sc., Foreign Member R.S.

There can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of whatever kind into liquids; and we ought not to despair of effecting it in low temperatures and by strong pressure exerted upon the unmixed gases.—JOHN DALTON (October, 1801).

An investigator should be almost a monomaniac, possessed of one idea only: to pursue and try to achieve but one purpose, and nothing else. Then, whether he makes a new discovery or not, he will have found satisfaction. But in no other case.—H. KAMERLINGH ONNES.

Je pense que tous ceux qui, en collaboration avec M. ONNES, ont travaillé à Leyde y ont connu des jours heureux.—MADAME CURIE.

LADIES AND GENTLEMEN,—

In 1885 the celebrated Swiss botanist Alphonse de Candolle wrote his enthralling work " Histoire des Sciences et des Savants." He closed one of the chapters of this book—the one in which, with the materials then at his disposal, he indicated to the country of Huygens the place which, about 1870, it occupied in the domain of natural science—with these very reassuring words: " Si mon analyse est vraie, la Hollande se relèvera. L'éclipse actuelle serait momentanée, comme celle de l'Angleterre à la fin du dix-huitième siècle. . . . Il existe encore tant d'excellentes influences en Hollande, qu'on peut espérer raisonnablement un retour de l'ancien éclat scientifique du pays." (" If my analysis is true, Holland will rise again. The actual eclipse is but temporary as the one in England at the end of the 18th century. . . . There are still so many excellent influences in Holland, that one can reasonably hope for a return of the ancient scientific lustre of this country.")

When treating the problems studied by de Candolle, we should now choose other data and criteria, and consequently a new work like de Candolle's is at the present moment a desideratum; but so much is certain, the prophecy pronounced in the sentences quoted has completely come true. This is in no small degree owing to the man whom the Chemical Society elected to its honorary Fellowship in the year 1920, and whom other scientific societies in this country —to mention only the Royal Society and the Royal Institution— honoured with the highest distinctions.

The communications from the Physical Laboratory of the University of Leyden give us a clear insight into what Heike Kamerlingh Onnes has done for science. But the Jubilee Volumes dedicated to him by his friends and co-workers in 1904, in commemoration of the day when, twenty-five years before, he obtained his Doctor's degree, and in 1922, when he had held his professorate for forty years, are valuable documents in the history of science, which would make a Memorial Lecture superfluous had they not been published in a language which is spoken and read by few only.

Thus the task which has been laid on me becomes a labour of love, because I am allowed to sketch to you the life of my deeply regretted friend, and to recall to your memory some of his great deeds, deeds which signalise him as a man who must be numbered among the " primi inter pares " for all time.

First of all, a few particulars about the period prior to the day (November 11th, 1882) when he was appointed professor at Leyden; we may call this period his youth, for the new professor had not yet attained his thirtieth year. He liked to speak of his youth, of which he always retained the most pleasant memories.

" My father was the owner of a tile factory at Groningen (Heike was born there on September 21st, 1853) and was continually at work to develop his factory and to apply the newest machinery. In his spare hours in the evening he read much and I remember him, sitting before me with his favourite periodical, the *Revue des deux Mondes*. He liked to philosophise and to theorise, and in his walks with us—often with me alone; I was the eldest—many problems were considered and adapted to my level.

" And my mother? When I was sixteen and got up in summer at five o'clock to prepare my school tasks, I often found mother at work in the garden. She had artistic tastes; her father had been an architect.

" My parents had not much intercourse with other people. The business men had different tastes, liked a good dinner, were not averse to a good glass, and talked shop. Among the men of science (Groningen is a university town) my parents had few friends. Therefore we remained at home, read much, talked about art, and developed ourselves consciously, so to say. It was our delight to go for long walks in the country. Sport, as we understand the term now, was hardly known; nowadays for many young people sport is an intentional aim.

" In my parents' house all was made subservient to *one* central purpose: to become *men*. And only when a deep inner culture goes hand in hand with refined good breeding, so that nothing is neglected, and manifests itself also in neat and careful dress, may we expect that the result of such an education will be to form men, in the best and widest acceptation of the word. Has it not been a blessing that I was educated in a family where such ideas obtained?"

In September, 1865, Heike became a pupil of the Hoogere Burgerschool at Groningen, a school which in many respects may be compared to the American High School. The registers of the school relate, not in dry figures, but in glowing terms, that Heike always excelled in zeal, assiduity and knowledge. And also among his school fellows—than whom there are no better judges—the memory lives that Heike was the cleverest pupil of the school. At the time the director was van Bemmelen, later on Professor of Chemistry in the University of Leyden, and Onnes has expressed in feeling terms his gratitude for the influence which van Bemmelen exercised on his pupils.

The school records further tell us : September, 1869, removed to the fifth class (the highest); passes an excellent final examination in 1870; matriculates a short time afterwards to study science at the University.

Our student soon showed that he knew how to combine business with pleasure by joining the Groningsch Studentencorps (Corporation of Students). His club fellows quickly became aware that Heike had completed a great part of his daily task when they had hardly awakened from their sleep. When, in March, 1871, the Utrecht University opened the envelope containing the name of the prizeman to whose essay: "A Critical Investigation of the Methods of Determining Vapour Density and of the Results obtained thereby, with respect to the Relation of the Nature of the Chemical Compounds and the Density of their Vapours," the gold medal had been awarded, the name proved to be

HEIKE KAMERLINGH ONNES
Student in the University of Groningen.

The writer had not yet attained his eighteenth year.

From the way in which the subject matter of this prize essay was treated we see that Onnes was attracted by the study of chemistry, but his inclinations evidenced themselves more clearly after his cand. phys. examination (November 9th, 1871), which he passed with honours; he resolved to leave the country for some time and follow a course of studies with that master-mind in Chemistry who had reaped so many laurels on the banks of the Neckar. So he passed the winter term of 1871 at Heidelberg with Bunsen, the physico-chemist by the grace of God whose humorous sayings were well known to many generations of students and still form the lighter side of the literature of science.

Was it Bunsen's calorimetric investigations, published in 1870, which drove Onnes in 1871 to the birthplace of spectrum analysis? These investigations led to the rediscovery of the ice-calorimeter, which had already been described by Hermann of Moscow in 1834.

Certain it is that our student showed great interest in calorimetric methods in general. This is seen from his essay written in answer to a prize question from the Senate of the State University at Groningen : " A Critical Survey of the Methods of Determining the Quantities of Heat which are set free by Chemical Reactions and Dissociations and of the Results obtained by Different Investigators." Although for this essay Onnes got a silver medal (October 10th, 1872), the opinion of the Senate is not unqualified : " several times serious physical and chemical errors are found," but, on the other hand, it is stated " that he often shows great ingenuity and clever resourcefulness."

Soon we see his inclination for physics cropping out more strongly. At first he worked under the guidance of Bunsen and Kirchhoff; later on, we find him more frequently in the laboratory of Bunsen's friend and co-worker, of the man of whom A. W. von Hofmann said : " Auf meinem langen Lebenspfade bin ich keinem begegnet, bei welchem, wie bei Kirchhoff, höchstes Vollbringen gesellt gewesen wäre mit fast demutsvoller Bescheidenheit." (" During my long life I have never met anyone who, like Kirchhoff, joins the highest power of performance to almost meek humility.")

The " Seminarpreis," awarded to our candidate, which was a great honour, enabled him to work in Kirchhoff's laboratory, a privilege which was granted to two students only. Here Onnes gave himself heart and soul to experiments with Foucault's pendulum, and this investigation became later the starting point for his thesis (" New Proofs for the Axial Changes of the Earth "), which he wrote in his own country. One needs only to glance at the preface of this thesis to see how gratefully the author recalls the time spent at Heidelberg, guided by the man who not only had opened new worlds to mankind, but who had also been endowed with a talent for theoretical and practical investigation, and was a first-rate teacher besides.

Onnes's wanderings ended at the close of his stay at Heidelberg (April, 1873), where Gabriel Lippmann and Arthur Schuster were among his fellow-students. On his return to his native town Professor R. A. Mees became his mentor.

The fact that our student twice obtained the prize for an essay must not lead to the erroneous idea that he belonged to the genus of " plodders." In the Students' Almanacs of the Groningen University mention is made of the fact that Onnes was a very good horseman, and so well liked by his fellow members of the Students' Corporation that they elected him Rector. In their club building, Kamerlingh Onnes's memory is perpetuated by a memorial stone, on which his name is carved, placed there by the gratitude of his fellow members for the fact that it was especially owing to Onnes's organising talents that the building was brought under direct management. We also read in those annals of students' joy and students' grief that the then Rector took an active part in the movement against a Government measure, at that time under consideration, to abolish the Groningen University.

On June 6th, 1876, Onnes passed his "doctoraal" examination with honours, but the last stage in his academical studies, his Doctor's degree, to be got after he had maintained a thesis, only came a few years later. This is not to be wondered at when we consider the size and the subject of his thesis, which he maintained on Thursday, July 10th, 1879, at Groningen. The Faculty thought its contents and treatment so excellent that they did not require the candidate to leave the room at the end of the examination, as is the custom in Holland, but unanimously and without discussion awarded him the Doctor's degree with great honours (magna cum laude).

When we read the preface of this thesis attentively, we find in it the programme which the young scientist had traced for himself, a programme to which he adhered to the end of his days. "When writing this thesis," he says, "I always tried to take to heart the lesson which the young student in science may find in the Memorial Lecture on Gustav Magnus, written by Helmholtz: 'Gegenwärtig scheint es mir, als wenn immer mehr und mit Recht die Ueberzeugung Boden gewönne, dass in dem entwickelteren Zustande der Wissenschaft nur *derjenige* fruchtbar experimentieren könne, der eine eindringende Kenntnis der Theorie hat und ihr gemäss die rechten Fragen zu stellen und zu verfolgen weiss; und andererseits, dass nur *derjenige* fruchtbar theoretisieren könne, der eine breite praktische Erfahrung im Experiment habe.' ('It seems to me that nowadays the conviction gains ground that in the present advanced stage of scientific investigation only *that* man can experiment with success who has a wide knowledge of theory and knows how to apply it; on the other hand, only *that* man can theorise with success who has a great experience in practical laboratory work.')"

Before taking his doctor's degree, Onnes had fixed his abode in the town where van Leeuwenhoek had lived, and where he filled the post of assistant in Bosscha's laboratory (1878). The four years he spent there were years of hard work; he was required to give Professor Bosscha's course of lectures, and his laboratory work was an excellent training for the future experimenter, as he himself testifies at a later period. The reports of the annals of the students, who were not accustomed to make a secret of their opinions, show us how much his lectures were appreciated by his audience.

A scientist with a career like Onnes's was obviously the right man to fill the vacancy caused by the retirement of Ryke, professor of experimental physics at Leyden. So we see Onnes, on October 11th, 1882, in the Hall of the University, in the chair, to deliver his inaugural lecture in which he sketched the importance of quantitative investigation in physics. This day was the beginning of a new period in his life, but it was also for Onnes the dawn of his triumphal progress through the realm of low temperatures.

Time is lacking to describe this triumphal progress in detail. But for one short moment I wish to dwell on the above-mentioned lecture of 1882 and on the one delivered by Onnes as "Rector Magnificus" of the University of Leyden: "The Importance of Accurate Measurements at very Low Temperatures." Even at the present day these addresses have a great fascination for the reader. We do not know which excites our admiration more: his prophetic eye or the unequalled energy he displayed at a ripe age in accomplishing the programme he had at one time evolved. If we want completely to understand the contents of these addresses, we must first of all try to realise the progress of physics, especially of thermodynamics, about 1875.

Two years earlier a man had obtained his doctor's degree at Leyden, after maintaining a thesis: "On the Continuity of the Gaseous and Liquid States," whose work elicited a year later the remark of Clerk Maxwell (in a lecture delivered to this Society on February 18th, 1875): ". . . but his attack in this difficult question is so able and brave that it cannot fail to give a notable impulse to molecular science. It certainly has directed the attention of more than one inquirer to the study of the Low-Dutch language in which it is written."

We know now, from a letter from Andrews at Belfast to James Thomson (February 5th, 1874), that this view was correct: "P. S. Bessie and I are hard at work on Diderik van der Waals," and a few months later Andrews writes: "My dear Thomson. . . . I am deep in the Dutch paper and also occupied with my own results, which I believe will turn out more important than I supposed. But I miss you sadly."

Fourteen years later the paper of van der Waals was translated into English under the auspices of the Physical Society in London.

The experimental testing of the equation of state, given by van der Waals in his thesis, together with the one of the law of corresponding states, published by van der Waals in 1880, formed the first part of Onnes's programme.

In later years he tells us: "This law had a special charm for me, because I was of opinion that it was based upon the stationary mechanical similitude of the substances considered. From this point of view the study of the divergences in substances of simple chemical structure with low critical temperature seemed to me of great importance. Precision measurements at low temperature must be very attractive in my opinion. For this purpose, it was necessary to dispose of large apparatus with which the measurements could be made at a constant temperature, and it was indispensable to construct suitable temperature baths, baths which could also be used for numerous other investigations."

Thus, as soon as Onnes had entered upon his new sphere of activity, the foundations were laid of an institution in which the investigations in question could be taken in hand—the Cryogenic Laboratory of Leyden, which, in consequence of the results attained, was soon to become an international centre of research.

The efforts of Onnes and his co-workers met with stupendous success. In 1904 liquefied air and oxygen formed the boundary line of the low temperatures which could be obtained with cryostats; two years later hydrogen could be made in large quantities. Eight years before, Dewar had liquefied this gas in the laboratory of the Royal Institution in this city. The reason why so much time elapsed between the moment when Dewar could wire to Onnes: "Hydrogen liquefied," and the application at Leyden was that Onnes wanted to have at his disposal large quantities of liquids for his cryostats.

When we read the papers on the investigations in the Leyden Laboratory we are struck again and again by the great appreciation which Onnes had for the men who were working in the domain which he had chosen for his life-work, and he continually admits that he owes much to their researches. In his address of 1904 he says: "In the meantime, an entirely new path has been struck by Dewar with respect to investigations at low temperatures. He taught us to make glass vessels, beakers, bulbs, and glasses in which liquids with boiling points at very low temperatures could be kept and transported. These vacuum vessels have double walls which are silvered on the inside, whilst the space between them is exhausted to the utmost. The access of heat from without is now diminished to such a degree that the liquid does not evaporate perceptibly. By means of this invention we gained the desired free disposal of refrigerants like liquid oxygen. Dewar's magnificent invention may be called the most important appliance for operating at extremely low temperatures. The open vacuum flasks are for the permanent gases what the steel bottles, tested at 250 atmospheres, are for the coercible gases. In fact, the moment when a vacuum glass containing liquid oxygen was offered to the Prince of Wales at the meeting of the Royal Institution marks a new era in low-temperature research."

The words which Henry E. Armstrong used in his most fascinating address dedicated to the memory of James Dewar may be unconditionally applied to Onnes: "His object was never merely to liquefy gases. He was never the mere artificer, but always the philosopher seeking to penetrate into the far distant region of the ultimate zero of temperature." This very fact made Onnes's creation at Leyden the place where investigators from all parts of the world could carry on their research work. Thus this building, distant but a few steps from the spot where, two centuries before, Boerhaave had expounded to his students Boyle's "Experimental History of Cold," became the place where physics in their entirety, physical chemistry, physiology, could be studied at the lowest point of temperature.

"Wer zählt die Völker, nennt die Namen,
Die gastlich hier zusammen kamen?"

("Who counts the nations or knows the names of all who were hospitably received here?")

These words of the poet would make a suitable inscription, not only for the Cryogenic Laboratory, but also for Onnes's artistic house, where so many scientists could and did find relaxation from their strenuous labours.

Science owes much to Lavoisier's wife for the share she took in her husband's work, but no less praise is due to Elisabeth Byleveld, who, since September, 1887, shared the sweets and bitters of Onnes's life. Besides her duties as a mother, which she fulfilled with the greatest tenderness, she always guarded her husband from the troubles of daily life as much as lay in her power and she took the greatest care of his ailing health. Onnes himself says: "She has toiled for me, has always been ready to put her own wishes in the background, has received my guests, and taken care of them."

All who have stayed in her hospitable home know that when her husband had finished his daily task in the hyper-arctic regions of science, he found in her companionship the warmth necessary to stimulate his energy for new problems. And new achievements were not wanting, even up to the last days of Onnes's life; the unending flow of communications from the physical laboratory of the University of Leyden testifies this. In these communications are the results of thermodynamic, magnetic, magneto-optical, radioactive and electric investigations at the lowest temperatures. In this hour I recall to your memory one of the most remarkable and far-reaching achievements of Onnes and his staff, the one which more than any other entitles him to the epithet of "gentleman du zéro absolu." The day is December 10th, 1913, the anniversary of the death of Alfred Nobel. A select crowd has met in the Great Hall of the Royal Academy of Music at Stockholm, where those to whom Nobel prizes have been awarded are to receive the insignia from the hands of the King of Sweden. As is seen from the following lines, Onnes is among the laurelled :

HEIKE
KAMERLINGH ONNES

for hans undersökningar öfver kroppars egenskaper
vid läga temperaturer hvilka bland annat ledt till
framställningen af flytande helium.
Stockholm den 10 December 1913.
TH. NORDSTRÖM,
Kungl. Vet. Akad-s preses.
CHR. AURIVILLIUS,
Kungl. Vet. Akad-s sekreterare.

(For his investigations on the properties of substances at low temperatures, which investigations, among other things, have led to the liquefaction of helium.)

The next day he mounted the platform and sketched the "Leiden und Freuden" (disappointments and joys) of the years that lay behind him. After pointing out that the theories of van der Waals and more particularly his "law of corresponding states" had guided him, he surveys the results attained by Wroblewsky, Olszewski, Pictet, Linde, and Dewar at low temperatures, and in imagination he leads his audience through the Leyden Cryogenic Laboratory. He introduces them to his numerous co-workers, among whom Crommelin has especially distinguished himself in the technical part of the work, and finally depicts to them the way in which helium was liquefied : "The limit of what was possible was reached, as had been foreseen when the plans were formed. The experiment (July 10th, 1908) began at half past six a.m. and ended at half past nine p.m. When at half past six p.m. the first liquefied helium was perceived, not only had the apparatus been strained to the uttermost, but the utmost had also been demanded from my assistants. But for their perseverance and their ardent devotion, every item of the programme would never have been attended to with such perfect accuracy as was necessary to render this attack on helium successful. In particular I wish to express my great indebtedness to Mr. G. J. Flim, who, as chief of the technical department of the Cryogenic Laboratory, not only assisted me in leading the operations, but also superintended the construction of the apparatus according to my direction and rendered me the most intelligent help in both respects.

"It was a wonderful moment when the liquid, which looked almost immaterial, was seen for the first time. It had not been perceived when it flowed into the glass; its presence could be detected only when the glass had been filled. Its surface stood out sharply defined like the edge of a knife against the glass wall. I was overjoyed when I could show liquefied helium to my friend van der Waals, whose theory had been my guide in the liquefaction up to the end."

And when, later on, Onnes himself relates that on this memorable day his wife fed him, beginning at three o'clock, by putting bits of bread into his mouth, there rises up before us the image of Caroline Herschel, your compatriot, who read to her brother, Sir William, when he was polishing his mirrors, and—to use her own words—"was constantly obliged to feed him by putting the victuals by bits into his mouth."

But, Ladies and Gentlemen, read the "Communications" for yourselves; the description of the journey to the nadir of temperature, and especially the famous discovery by Onnes (1913) of the supra-conductivity of metals at very low temperatures, will awaken your interest as much as the most thrilling novel. According to the electron gas theory of metallic conduction, one might have expected that the resistance of a metal would diminish continuously with fall of temperature, or even that the resistance at very low temperatures might begin to rise sharply, owing to a sort of freezing of the electrons. Onnes made the startling discovery that the resistance of certain metals suddenly falls to zero (or to an extremely low value, at a temperature varying with the nature of the metal) a few degrees above the Kelvin zero point.

Even before the verdict of the scientific world had assigned the Nobel prize to Onnes, Dutch scientists had given him a token of their profound veneration. Not one of the numerous company which had gathered in the Great Hall of the Amsterdam University on November 18th, 1908, on the occasion of the Annual General Meeting of the Ancient Association of Physics, Medicine, and Surgery, but will think with emotion of an event in the history of science at which he was then assisting. For on that day van der Waals and Kamerlingh Onnes were to be given a mark of the high appreciation which was felt by the whole scientific world; to each of them was to be presented the medal of honour, the highest mark of distinction at the disposal of the Association, to Onnes for the liquefaction of helium, to van der Waals for his "law of corresponding states."

"Expressed in mathematical terms," thus van der Waals addressed Onnes, "this law may be formulated in this way: If we consider different substances at temperatures which are an equal number of times their critical temperatures, and under pressures which are an equal number of times their critical pressures, the volumes are each an equal number of times the critical volume.

"Elsewhere I have expressed this differently, in words that can be more easily understood: all substances form one single genus. If we compare, for instance, height with temperature, breadth with pressure, and length with volume, we can say that all substances are copies of one another. If one substance has a critical point, such a point must appear in all the others. But whereas, in individuals belonging to the same genus, the differences in height, breadth, and length are but slight, these differences may be very great with temperature in the different substances. Thus the critical temperatures sometimes diverge in the proportion of 1 to 1000.

"Now it was a question whether helium, the discovery of which has taken place in recent years only, also belongs to this common genus, whether this dwarf also has a well-formed shape. We owe it to you, highly esteemed Kamerlingh Onnes, that now we know this for certain. Only you could investigate it in your cryogenic laboratory, which is unequalled for organisation. You conducted this investigation systematically. By carrying out measurements of pressure and volume at the lowest possible temperature, you were able to determine the so-called Boyle point, *i.e.*, the temperature at which, with very great volume, the substance follows Boyle's law. For all substances, the Boyle point is rather more than three times higher than the critical temperature, according to the equation of state 27/8 times the critical temperature.

"Strictly speaking, the question was now settled: Helium too possesses this very same remarkable point; moreover, the critical temperature of helium, being rather more than three times lower than the Boyle point, was also known. Dewar had already announced that helium has a reversion temperature for the Joule-Kelvin effect. But this lies rather more than six times higher than the critical temperature. So you had halved the distance which separated actual results from the critical temperature of helium. But you would not stop here; you wanted to see not only the front and face of the well-formed shape, but its heart also. You wanted to reach the critical temperature itself and to liquefy the substance. And on the memorable 10th of July, after a long day's work, surrounded by a staff of well-trained observers, you achieved it after careful preparation.

"First of all, you deduced, from the value found for the Boyle point, that the critical point would lie about 6° above absolute zero. Then, assuming the well-formed shape, you calculated how much helium you would require, considering the size of your apparatus, to what temperature you would have to cool it at first by means of hydrogen, and to what pressure you would have to submit it, so that by free expansion it could cool itself to below 6°. Having considered everything, you worked the summer day through, until, long after sunset, you succeeded in liquefying helium. You have made it possible to approach much closer to the absolute zero than could be done up to this time, an achievement which is of the highest importance for many scientific problems in which the influence of low temperatures has to be studied.

"It is therefore with a feeling of admiration for the results you have attained, with a feeling of veneration for your character as a man and an investigator, with a feeling of gratitude on account of science in Holland—because, as Korteweg said at the Royal Academy of Sciences, you have made the heart of every Dutch scientist thrill with joy and with a feeling of warm friendship—that I present to you this commemorative medal in the name of the Association for the Advancement of Physics, Medicine, and Surgery."

Van der Waals spoke a true word when he gave utterance to his feelings of veneration for Onnes's character as a man and an investigator. An incident in the previous history of the liquefaction of helium proves this, an incident which should serve as an example for all scientists: On March 5th, 1908, Onnes wired to Dewar in London: "Converted helium into solid. Last evaporating parts show considerable vapour pressure, as if liquid state is jumped over." On April 16th, Onnes wrote to the editor of *Nature*: ". . . The prosecution of the experiments has shown that what I observed in expanding the gas was *not* the evaporation of *solid* helium, but solution phenomena of solid hydrogen in gaseous helium. I have communicated to the Amsterdam Academy a note on my experiments, which at the moment leave the condensation of helium a yet undecided question." With unflagging zeal Onnes set to work again: on July 10th of the same year the problem was solved: helium had been liquefied.

The results attained could not but stimulate our untiring investigator to new labours. First and last his maxim is "*Inferior!*"

In a paper "On the Lowest Temperature yet obtained. An Introductory Paper to a General Discussion on the Generation and

Utilisation of Cold," read before the Faraday Society and the British Cold Storage and Ice Association on Monday, October 16th, 1922 (proof subject to revision), he summarised his newest conquests in the words : " Taking into account the uncertainty of the extrapolation, it will be better to say that the lowest temperature yet attained is some hundredths of a degree below 0·9K."

Onnes was obliged to leave the last stage of the work on which he had set his heart, the solidifying of helium, to one of his most brilliant pupils, whom he also recommended as his successor. At least five times (for the first time in 1908) Onnes tried to attain the result, but he never succeeded. Only a few months after his death (he passed away on February 21st, 1926) this refractory substance was subjugated by Keesom.

The plans which Onnes had already formed when he became professor at Leyden and grew to greater proportions as his work progressed ("Es wächst der Mensch mit seinen grössern Zwecken" . . . man grows with his growing projects . . .) required, not only a talented experimenter, but also a man with great organising ability. And Onnes had been gifted in this respect also. As such he rendered an invaluable service to the craft of instrument-making by founding the Society for the Promotion of the Training of Instrument-makers (1901). He gave new life to the traditions which arose in the workshop of van Mussenbroek Brothers at Leyden as early as the 17th century. Scientists constantly demand better instruments by means of which they can penetrate into the heart of Nature, and consequently greater demands are made on the makers of these appliances. Onnes's training school for instrument-makers, annexed to the Cryogenic Laboratory, was not only a training school for his own mechanics by which he was enabled to surmount many difficulties that presented themselves in his investigations; it became an establishment at which the laboratories in Holland have an excellent opportunity of providing themselves with first-rate workmen, and which has given many an excellent instrument-maker to the laboratories in Europe as well as to institutions beyond the Atlantic.

From what I have told you about Onnes's work you must have gathered that what he accomplished may be considered a stupendous achievement even for a man in normal health. Such a task is the more remarkable because Onnes had always to contend with his bronchial weakness. It is sad to read in the letters which he wrote from time to time to his friend van der Waals how much he was handicapped by his weak health, but the indomitable energy which urged him on to new problems awakens our admiration. Notwithstanding these reverses, which often retarded the progress of his work, he was always happy. To van der Waals he wrote on September 11th, 1912, a few days after his silver wedding:

LEYDEN, *Sept.* 11*th*, 1912.
HUIZE TER WETERING.
HAAGWEG.

"DEAR FRIEND,—We deeply regretted that you could not come to Leyden yesterday as we had so much hoped. We should have liked to thank you in person for the kind letter, written in the name of all of you, and for the fine flowers with which you added lustre to our reception. For the time being, our room was a flower garden for the bride at her silver wedding.

"Our silver wedding was an event the commemoration of which had for a long time been looked forward to as a day which would fill us with heartfelt thankfulness for the many blessings we had received in the twenty-five years which lie behind us. So you will understand that we celebrated this day with thankful hearts and that we shall always look upon it as a pleasant milestone on the road which lies behind us.

"Which of us, Betsy,* Albert,† or myself, was most affected by these feelings is hard to say. All of us are equally conscious that our gratitude can never be great enough for the supreme happiness and prosperity which have been showered upon us. As for the prosperity, the measure of it can be realised best by me, because after our marriage the cares which I had known before diminished. When I re-read mother's letters, written in those most care-ridden years, it is as if I look back upon a totally different world, and it seems to me that only now I realise how appalling were the difficulties with which we had to contend—always hopefully after mother's example—until at last they gave way. When I think of that time, our present prosperity makes me doubly thankful. And as for the happiness we enjoy, although it has been mixed with affliction—the sad loss of our parents is still a source of sorrow—we have been favoured above many, because we have been allowed to possess them for so long a time in mutual love. And while gratefully accepting all this abundant happiness, a feeling of modesty and diffidence comes over us. When we thought of our future we felt the need of lifting up our hearts, and therefore we were deeply moved when Albert, who executed the recitative, and Harm ‡ with the two nieces who accompanied, received us at breakfast in the family circle of brothers and sisters with a solemn aubade.

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* His wife. † His son. ‡ His nephew.

"May your wish 'that we shall long be spared for each other, every one of us labouring to the best of his ability'—which is also our fervent hope—be fulfilled. Once more our best thanks, with cordial greetings from all to all. In the name of our old friendship,

Cordially yours,
H. KAMERLINGH ONNES."

All who realised the important part which nowadays is played by temperatures below freezing point welcomed with satisfaction the co-operation between technics and science which was brought about by the institution of the "Association internationale du Froid" (1909), in which Onnes also took an active part. About ten years later it was reconstructed under the name of "Institut international du Froid." It was there that for the first time the epithet of "gentleman du zéro absolu" was applied to Onnes, whilst in his own country his popularity appears from a cartoon in which he is given the sobriquet of the "Freezer." Whoever reads the annual reports of the "Institut international du Froid" will agree that, contrary to the prevailing idea, low temperature had not impaired Onnes's energy and rate of reaction when it was necessary to promote the interests of the Institute. Is it to be wondered at that numerous learned Societies in his country and abroad, borrowing Saurin's line under the bust of Molière :

"Rien ne manque à sa gloire, il manquait à la nôtre"

have awarded their highest distinctions to Onnes. This was done also by this Society. He valued such marks of distinction very much, as may be seen from a passage in a letter to his friend van der Waals, in which he congratulates him on his election as corresponding member of the French and Prussian Academy of Sciences. Onnes says : ". . . the proof that slowly your work is being understood must be a source of great satisfaction to you."

At the commencement of my discourse I mentioned the beautiful international Jubilee volume which was presented to Onnes on November 11th, 1922, on the occasion of the fortieth anniversary of his professorate. On that memorable day all vied with one another as to who should be the first to show him, beside appreciation of his scientific labours, admiration for his amiability which had engendered love in the hearts of all who made his acquaintance. The staff of his laboratory, too, wished to give expression to their feelings. When visiting the Cryogenic Laboratory at Leyden, you will notice a memorial stone of grey marble, in which are carved these words:

> "On this spot, on the 10th of July, 1908, Helium was liquefied for the first time by Dr. HEIKE KAMERLINGH ONNES.
>
> The entire staff of the laboratory has presented to him this memorial on the occasion of the 40th anniversary of his professorate.
>
> November 11th, 1922."

On this festal day an amazed audience admired the rare phenomenon of a fountain of liquid air. And, while reminding you of that day, I must not omit to mention the words spoken by Onnes about the cordial relations that existed between him and H. A. Lorentz:

"Now that I am speaking about friendship," thus he said, "I also think of my older friend Lorentz. We began our studies at the same time, and I can glory in a friendship of more than fifty years, a friendship which was shared by our mutual households. It has always been a great privilege to work with such a man as Lorentz. First he preserved my health by giving several of my lectures, which had the additional advantage of allowing me more time for my work in the laboratory. And later on, when he was called to Munich, it was by his efforts that Kuenen came here, who, as I have said before, succeeded in making the laboratory for the greater part what it actually is."

It is as if I still hear his voice when, on February 8th of last year, one day before my departure for America, he telephoned to me, wishing me a prosperous voyage and expressing the hope to see me again in good health on my return. Fortunately, he was spared a long sick bed; no sooner had I set foot ashore on the other side of the Atlantic than the sad tidings of his death reached me.

When we see how scarce really noble characters are among the living, and, on the contrary, how plentiful among the dead, according to biographies and epitaphs, we cannot wonder that the world in general refuses to believe in the existence of such characters, either among the living or the dead. And yet in Kamerlingh Onnes we had a man in whom it is difficult to discover qualities which one would have wished different. He was not only the "gentleman du zéro absolu," but, as my friend Donnan has said, "a gentleman in every sense of the word, and one of the first gentlemen of European science."

Thus Kamerlingh Onnes has lived his life—a life, although long, yet too short for my friend himself, too short for his family, too short for science. Many blessings fell to his lot and, although grief was not spared him, the benefits prevailed. He found love and friendship; he had an intellectual life, rich in discoveries, as is given but to few. Love, friendship, discoveries, and also honour. For Kamerlingh Onnes was not one of those whose merits are recognised at a ripe age only. He was an unknown scholar for but a short number of years. Very soon his life became one triumphal progress. And is it not his greatest triumph that in spite of all the marks of esteem which were showered upon him by all the world he remained a simple, genial, and kind-hearted man.

CLXV.—*Aminobenzthiazoles. Part IX. The Unsaturation of Aminobenzthiazoles containing a Static Triad System, and the Synthesis of some* 1-*Dimethylaminobenzthiazoles.*

By ROBERT FERGUS HUNTER and ERIC ROFE STYLES.

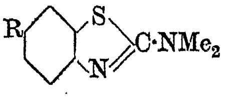
IT has been suggested (Hunter, J., 1926, 1385; Hunter and Soyka, *ibid.*, p. 2959) that the production of isomeric bromides from aminothiazoles containing a mobile amidine system [H]N·C:N $\rightleftharpoons$ N:C·N[H] is due to the addition of bromine to the tautomeric forms of the triad system. It being obviously desirable, therefore, to examine static derivatives (I) in which both mobile hydrogen atoms have been alkylated, the bromination of certain *s*-aryldimethylthiocarbamides and 1-dimethylaminobenzthiazoles was undertaken.

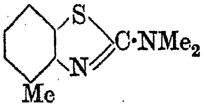
On bromination in chloroform, *s*-phenyldimethylthiocarbamide readily gave a *dibromide* of 1-dimethylaminobenzthiazole, which yielded the dimethylaminobenzthiazole (I; R = H) on reduction in the usual way (*loc. cit.*). A well-defined *pentabromide* of the dimethylamino-base was sometimes isolated, which was probably the hydrobromide of the tetrabromo-addition compound of the base. The bromination of *s*-phenyldimethylthiocarbamide, however, proceeded less readily than that of phenylthiocarbamide and of *s*-phenylmethylthiocarbamide (J., 1926, 1385), and this is probably due to the fact that in phenylthiocarbamide the mobile triad system [H]N·C:S $\rightleftharpoons$ N:C·S[H] is duplicated in such a way as to favour the production of the thioamide phase of the thiocarbamide, through which thiazole ring formation takes place by way of a labile ·CBr–SBr derivative (Hunter and Soyka, *loc. cit.*). In any case, some *s*-phenyldimethylthiocarbamide was recovered unchanged under conditions in which phenylthiocarbamide was completely transformed into 1-aminobenzthiazole dibromide.

On bromination in chloroform with excess of bromine, 1-*dimethylaminobenzthiazole* readily yielded a well-defined *hexabromide* (compare Hunter, J., 1925, **127**, 2271, and later papers).

The bromination of s-o-*tolyldimethylthiocarbamide*, however, gave rise to a well-defined, stable *tetrabromide* of 1-dimethylamino-3-methylbenzthiazole, which yielded the 3-methyl base (II) on

(I.)





(II.)

reduction in the usual way. This tetrabromide only lost bromine on exposure to moist air for several weeks, and it must be assumed that the instability produced in the NBr_2 complex by the *o*-methyl group (Hunter, J., 1926, 1401) is more than neutralised in the presence of the μ-NMe_2 group. This suggested that the bromides of the 5-substituted 1-aminobenzthiazole bases prepared by Dyson, Hunter, and Morris (preceding paper) might be greatly stabilised, and thereby rendered more readily comparable, by dimethylation of the amino-group, and the bromides of the 5-substituted 1-dimethylaminobenzthiazole bases (I) were therefore studied. In every case, bromination of the *s*-*p*-substituted phenyldimethylthiocarbamide gave rise to the bromide of the corresponding dimethylaminobenzthiazole, and these compounds differed strikingly from the bromo-addition compounds described in the preceding paper as regards their stability to moist air; on reduction, they all yielded the corresponding 5-substituted bases (I) in the usual way.

s-p-*Methoxy*- and s-p-*ethoxy-phenyldimethylthiocarbamide* yielded the tetrabromides of 5-methoxy- and 5-ethoxy-1-dimethylaminobenzthiazole, respectively. p-*Tolyldimethylthiocarbamide* resembled phenyldimethylthiocarbamide and gave rise to a *pentabromide* of 1-dimethylamino-5-methylbenzthiazole, which was very probably the hydrobromide of the tetrabromide. Bromination of 1-dimethylamino-5-methylbenzthiazole (I; R = Me) gave rise to a *hexabromide* of this base. p-*Chlorophenylthiocarbamide*, however, on bromination under the usual conditions yielded a *tribromide* of 5-chloro-1-dimethylaminobenzthiazole which was probably the hydrobromide of the dibromo-addition compound of the 5-chloro-base.

In view of the alternation of hexabromides and tetrabromides in the ascending homologous series of 2-alkylamino-β-naphthathiazole bromides (Dyson, Hunter, and Soyka, J., 1926, 2965), the bromination of s-α-*naphthyldimethylthiocarbamide* was also studied. As might have been anticipated, this thiocarbamide gave rise to the tetrabromo-addition compound of the naphthathiazole, which yielded 2-*dimethylamino*-β-*naphthathiazole* on reduction.

EXPERIMENTAL.

The *s*-aryldimethylthiocarbamides described below were prepared, in yields of 80—90%, by treating the arylthiocarbimides (preceding paper) (1 mol.) in alcohol (5 vols.) with a 20% excess of a 33% solution of dimethylamine in absolute alcohol; in each case the mixture was warmed, and then concentrated at 15°/20 mm. The thiocarbamides were usually recrystallised from absolute alcohol.

s-Phenyldimethylthiocarbamide crystallised in long prisms, m. p. 133° (compare Dixon, J., 1892, **61**, 539) (Found: S, 17·6. Calc.: S, 17·8%).

1-*Dimethylaminobenzthiazole Dibromide.*—A solution of phenyldimethylthiocarbamide (1 g.) in chloroform (10 c.c.) was slowly treated with 0·8 c.c. of bromine; a yellow precipitate (bromo-addition compound of the thiocarbamide?) formed, which redissolved with evolution of heat and hydrogen bromide. The mixture was refluxed for 5 minutes and concentrated. It could not be induced to crystallise * and therefore was evaporated in a vacuum at 15°. The red gum obtained, after remaining in an evacuated desiccator for 20 hours, solidified in small, hard, vermilion crystals of the *dibromide*; these, after being crushed on porous earthenware and dried in a vacuum over potassium hydroxide, melted at 91—93° (decomp.; reddening at 60—70°, softening at 75—80°) (Found: Br, 48·0. $C_9H_{10}N_2Br_2S$ requires Br, 47·3%). This compound had the usual properties and liberated iodine from dilute hydriodic acid (Found: Br, 40%).

1-*Dimethylaminobenzthiazole tetrabromide hydrobromide* (prepared from phenyldimethylthiocarbamide, 2 g.; chloroform, 20 c.c.; bromine, 2 c.c., in chloroform, 5 c.c.; time of refluxing, 15 minutes) separated, after the mixture had been concentrated in a vacuum at 15°/20 mm., in small, orange-red prisms, m. p. 101° (decomp.) after drying (Found: Br, 69·1. $C_9H_{10}N_2Br_4S,HBr$ requires Br, 69·1%).

1-*Dimethylaminobenzthiazole.*—Either of the preceding bromides was treated with a large volume of sulphurous acid (saturated with sulphur dioxide at 15°) and the filtrate therefrom was made strongly alkaline with ammonia (*d* 0·880); the base then crystallised in glistening flakes, m. p. 86°. After recrystallisation from alcohol it formed small, glistening needles, m. p. 87° (Found: S, 17·7. $C_9H_{10}N_2S$ requires S, 18·0%).

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* After this bromide had once been obtained crystalline, there was no difficulty in inducing subsequent preparations, made in the same laboratory, to crystallise.

1-*Dimethylaminobenzthiazole hexabromide* (prepared from dimethylaminobenzthiazole, 0·8 g.; chloroform, 15 c.c.; bromine, 1 c.c.) separated in orange-red, glistening plates, m. p. 211° (with efferv.) after being dried (Found: Br, 73·2. $C_9H_{10}N_2Br_6S$ requires Br, 73·0%).

s-o-*Tolyldimethylthiocarbamide* crystallises in shining prisms, m. p. 138° (Found: S, 16·3. $C_{10}H_{14}N_2S$ requires S, 16·5%).

1-*Dimethylamino-3-methylbenzthiazole tetrabromide* (prepared from *o*-tolyldimethylthiocarbamide, 2 g.; chloroform, 10 c.c.; bromine, 2 c.c., in 5 c.c. of chloroform; spontaneous boiling with evolution of hydrogen bromide; time of refluxing, 10 minutes) crystallised in orange-yellow, glistening prisms, which after drying had m. p. 160° (decomp.; softening at 125—130°, charring at 180°) (Found: Br, 62·3. $C_{10}H_{12}N_2Br_4S$ requires Br, 62·5%).

1-*Dimethylamino-3-methylbenzthiazole* was obtained by reduction of the tetrabromide with a large volume of sulphurous acid, and crystallised from alcohol in stellate clusters of glistening needles, m. p. 84° (Found: S, 16·4. $C_{10}H_{12}N_2S$ requires S, 16·7%).

s-p-*Methoxyphenyldimethylthiocarbamide* crystallised in glistening plates, m. p. 125° (Found: S, 15·3. $C_{10}H_{14}ON_2S$ requires S, 15·2%).

1-*Dimethylamino-5-methoxybenzthiazole tetrabromide*, obtained from 0·9 g. of *p*-methoxyphenyldimethylthiocarbamide in chloroform (6 c.c.) and bromine (0·9 c.c.), formed small, yellowish-orange plates, m. p. 195° (with efferv.) (Found: Br, 61·1. $C_{10}H_{12}ON_2Br_4S$ requires Br, 60·6%).

1-*Dimethylamino-5-methoxybenzthiazole* crystallised from alcohol in small, white prisms, m. p. 144° (Found: S, 15·1. $C_{10}H_{12}ON_2S$ requires S, 15·4%).

s-p-*Ethoxyphenyldimethylthiocarbamide* formed small, shining prisms, m. p. 163° (Found: S, 14·2. $C_{11}H_{16}ON_2S$ requires S, 14·3%).

1-*Dimethylamino-5-ethoxybenzthiazole tetrabromide* (prepared from the ethoxyphenyldimethylthiocarbamide, 1 g.; chloroform, 10 c.c.; bromine, 1 c.c.; time of refluxing, 2 minutes) separated in orange, glistening plates, m. p. 190° (decomp.) (Found: Br, 59·0. $C_{11}H_{14}ON_2Br_4S$ requires Br, 59·1%).

1-*Dimethylamino-5-ethoxybenzthiazole* crystallised in small prisms, m. p. 118° (Found: S, 14·1. $C_{11}H_{14}ON_2S$ requires S, 14·4%).

s-p-*Tolyldimethylthiocarbamide* crystallised in glistening plates, m. p. 169° (Found: S, 16·1%).

1-*Dimethylamino-5-methylbenzthiazole tetrabromide hydrobromide* was obtained from *p*-tolyldimethylthiocarbamide (2 g.) in chloroform (15 c.c.) and bromine (2 c.c.). After the mixture had been refluxed, and then concentrated in a vacuum for 2 minutes, the product crystallised in glistening, orange-red needles, m. p. 95° (decomp.; efferv. at 125°) (Found: Br, 67·8. $C_{10}H_{12}N_2Br_4S,HBr$ requires Br, 67·6%).

1-*Dimethylamino-5-methylbenzthiazole* separated from alcohol in small, glistening prisms, m. p. 86° (Found: S, 16·3%).

1-*Dimethylamino-5-methylbenzthiazole Hexabromide.*—One c.c. of bromine in chloroform (5 c.c.) was added to a solution of 0·9 g. of 1-dimethylamino-5-methylbenzthiazole in chloroform (15 c.c.); the hexabromide then separated in orange-red, glistening plates, m. p. 188° (decomp.) (Found: Br, 72·0. $C_{10}H_{12}N_2Br_6S$ requires Br, 71·4%).

s-p-*Chlorophenyldimethylthiocarbamide* formed small prisms, m. p. 152° (Found: S, 14·6. $C_9H_{11}N_2ClS$ requires S, 14·9%).

5-*Chloro*-1-*dimethylaminobenzthiazole dibromide hydrobromide*, obtained from 0·6 g. of *p*-chlorophenyldimethylthiocarbamide, suspended in chloroform (4 c.c.), and bromine (0·6 c.c.), crystallised in aggregates of orange-yellow needles, m. p. 264° (decomp.; sintering at 190°) (Found: Br, 54·6. $C_9H_9N_2ClBr_2S,HBr$ requires Br, 52·9%).

5-*Chloro*-1-*dimethylaminobenzthiazole* crystallised from alcohol in long, colourless prisms, m. p. 99° (Found: S, 15·0. $C_9H_9N_2ClS$ requires S, 15·1%).

s-α-*Naphthyldimethylthiocarbamide* crystallised in long prisms, m. p. 162° (Found: S, 13·8. $C_{13}H_{14}N_2S$ requires S, 13·9%).

2-*Dimethylamino*-β-*naphthathiazole tetrabromide* was prepared from the naphthyldimethylthiocarbamide (0·3 g.) in chloroform (3 c.c.) and bromine (0·3 c.c.) and formed a bright yellow, crystalline powder which sintered at 185° and melted at 225° (decomp. with charring) (Found: Br, 58·3. $C_{13}H_{12}N_2Br_4S$ requires Br, 58·4%).

2-*Dimethylamino*-β-*naphthathiazole* crystallised from alcohol in large, flat prisms having a yellow tinge; m. p. 138° (Found: S, 13·9. $C_{13}H_{12}N_2S$ requires S, 14·0%).

In conclusion, the authors desire to express their gratitude to Professor J. F. Thorpe, F.R.S., for his interest in these experiments, and one of them (R.F.H.) is indebted to the Ramsay Memorial Fellowship Trust for a Fellowship and to the Dixon Fund of the University of London for a grant which has defrayed the cost of some of the materials used in this work.

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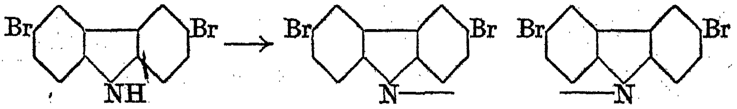
[*Received, December 30th, 1926.*]

CLXVI.—*The Dicarbazyls. Part II. 9 : 9′-Dicarbazyl and its Halogen Derivatives.*

By JOHN McLINTOCK and STANLEY HORWOOD TUCKER.

WIELAND and GAMBARJAN (*Ber.*, 1906, **39**, 1506) have stated that no bisdiphenylenehydrazine (9 : 9′-dicarbazyl) is produced when carbazole is treated with lead peroxide in benzene or with potassium permanganate in cold acetone, although both of these reagents act on diphenylamine giving tetraphenylhydrazine. Later, Perkin and Tucker (J., 1921, **119**, 216) obtained two crystalline dicarbazyls, A and B, and an amorphous product, C, by oxidising carbazole with potassium permanganate in hot acetone. The hydrogen atoms in the 9- and 3-positions of the carbazole molecule are the most reactive, and migration of groups from the 9- to the 3-position is common. Any method, therefore, which will prevent oxidation at one or other of these positions will tend to reduce the number and complexity of the oxidation products. It was with this idea in view that we attempted the oxidation of 3 : 6-dihalogen derivatives of carbazole, in the hope that oxidation would be confined to the imino-group.

When 3 : 6-dibromocarbazole was oxidised by the method of Perkin and Tucker (*loc. cit.*), a tetrabromodicarbazyl was produced. It was expected that, if this were a 9 : 9′-dicarbazyl derivative, it would reduce with comparative ease to 3 : 6-dibromocarbazole. The substance was very stable towards reducing agents, however, and likewise showed no tendency to dissociate (compare tetraphenylhydrazine). Reduction was eventually accomplished with hydriodic acid, carbazole only being produced. 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl* (II) was then synthesised as follows. 3 : 6-Dibromocarbazole (I), on treatment with finely divided potassium in benzene solution, gave a yellow potassium derivative, which was treated (without isolation) with iodine, (II) being produced.



(I.) (II.)

The oxidation product of 3 : 6-dibromocarbazole was found to be identical with (II).

Following on this, the first recorded synthesis of a derivative of 9 : 9′-dicarbazyl, we made attempts to isolate the unsubstituted hydrazine (9 : 9′-dicarbazyl). It seemed highly probable that one of the three compounds of Perkin and Tucker (*loc. cit.*) should have this structure. Accordingly, each was reduced with hydriodic acid, in order that some clue to its constitution might be obtained. Dicarbazyl A (m. p. 220°) gave only carbazole. Dicarbazyl B (m. p. 265°) gave a substance which we have not yet identified, while the amorphous product C (m. p. 175°) gave carbazole and a high-melting, unknown compound. Since 9 : 9′-dicarbazyl on reduction should give only carbazole, dicarbazyl A seemed the most likely to have this structure. This assumption was readily verified by the direct bromination of dicarbazyl A, 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl (II) being obtained.

The foregoing experiments were repeated, 3 : 6-di-iodocarbazole being used, and dicarbazyl A iodinated.

All attempts to synthesise 9 : 9′-dicarbazyl have met with failure. It has been shown (Wieland and Gambarjan, *loc. cit.*) that tetraphenylhydrazine may be converted into *NN*′-diphenylbenzidine by the action of cold concentrated sulphuric acid. The analogous conversion of 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl (Tucker, J., 1926, 3033) could not be brought about. *NN*′-Diphenylbenzidine is also obtained by oxidising diphenylamine in acid solution (Wieland, *Ber.*, 1913, **46**, 3296). This method of oxidation was applied to the 3 : 6-dihalogenocarbazoles in the hope that, since the 3 : 3′-compound could not be formed, a 1 : 1′-derivative might result. Only the 9 : 9′-dicarbazyl derivative was obtained, however, when acetic acid and sodium dichromate were used, whilst if sulphuric acid was present in the oxidising solution, a high-melting, amorphous substance was produced.

Attempts were made to oxidise 1 : 3 : 6 : 8-tetrabromocarbazole, by methods similar to those already described, with a view to obtain 1 : 3 : 6 : 8 : 1′ : 3′ : 6′ : 8′-octabromo-9 : 9′-dicarbazyl. The yield of the oxidation product was very small, however, and it is thought that the bromine atoms in the 1- and 8-positions must exercise some steric effect on the imino-group. This idea is substantiated by the fact that 1 : 3 : 6 : 8-tetrabromocarbazole could not be acetylated by the usual methods, nor could a nitroso-derivative be obtained.

The results obtained in the reduction of the amorphous substance C (Perkin and Tucker, *loc. cit.*) prompted some investigation into the structure of this compound, but so far the results have not justified us in assigning any formula to the substance.

EXPERIMENTAL.

3 : 6-*Dibromocarbazole.*—Some difficulty was experienced in obtaining this compound in quantity. The methods of List (Uerd. a. Rh. D.R.-P. 275,833) and of Mazzara and Leonardi (*Gazzetta*,

1895, **25**, ii, 397) were not suitable. A modification of Mazzara and Leonardi's method (*ibid.*, 1892, **22**, 569) was found to work fairly well, however.

(1) To a solution of 9-benzoylcarbazole (Stevens and Tucker, J., 1923, **123**, 2146; Tucker, *ibid.*, 1926, 546, footnote) (10 g.) in cold glacial acetic acid (140 c.c.), bromine (6 c.c.), dissolved in glacial acetic acid (10 c.c.), was added fairly rapidly. The product, which crystallised almost immediately, was removed after 3—4 hours, washed with a few c.c. of dilute alcohol, and crystallised twice from glacial acetic acid and once from benzene; 3 : 6-dibromo-9-benzoylcarbazole was then obtained in long, white needles, m. p. 213—214° (Found : Br, 37·9. Calc. : Br, 38·2%). The benzoyl derivative (2 g.) was hydrolysed by boiling it for $\frac{1}{4}$ hour with 5 c.c. of moderately concentrated alcoholic potash; short, white needles (from alcohol) of 3 : 6-dibromocarbazole, m. p. 211—213°, were obtained.

(2) A better method (similar to one described by Lindeman, *Ber.*, 1925, **58**, 2371), which we latterly used exclusively, was to brominate carbazole in carbon disulphide. Carbazole (50 g.) was dissolved in boiling carbon disulphide (600 c.c.), and a solution of bromine (34 c.c.) in carbon disulphide (130 c.c.) was added cautiously. The precipitated product was washed twice with cold carbon disulphide and crystallised twice from absolute alcohol; 3 : 6-dibromocarbazole, m. p. 211—213°, was then obtained (yield, 60%).

Oxidation of 3 : 6-*Dibromocarbazole.*—(1) *With potassium permanganate in acetone.** 3 : 6-Dibromocarbazole (5 g.) was dissolved in pure acetone (40 c.c.), finely powdered potassium permanganate (7 g.) added, and the solution boiled for 2—3 hours on the waterbath. The mixture was then poured into water, and sulphur dioxide passed through the suspension until there remained only a light reddish-brown solid, which was separated and extracted with boiling alcohol. The brown, alcohol-insoluble residue was crystallised twice from benzene, giving small, white cubes of 3 : 6 : 3′ : 6′-*tetrabromo*-9 : 9′-*dicarbazyl,* m. p. 249—250° (Found : Br, 49·2; *M*, cryoscopic in benzene, 629. $C_{24}H_{12}N_2Br_4$ requires Br, 49·4%; *M*, 648). This compound is very slightly soluble in alcohol, fairly easily soluble in acetone or glacial acetic acid, and very soluble in benzene, toluene, or xylene.

(2) *With sodium dichromate in acetic acid.* 3 : 6-Dibromocarbazole (2 g.) was dissolved in glacial acetic acid (40 c.c.), and sodium

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* The acetone used in the oxidations described was purified by boiling it (2 l.) with powdered potassium permanganate (20—30 g.) for 1 hour. The acetone was recovered by distillation through a long column, the fraction, b. p. 55—57°, being retained for use.

dichromate (0·4 g.), dissolved in water (0·5 c.c.), was added. The green solution was boiled for ¼ hour and poured into cold water, and the pink precipitate so produced was removed, thoroughly extracted with boiling alcohol (three times with 20 c.c.), and then crystallised twice from benzene. Small, white cubes of 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl, m. p. 249—250°, were obtained.

(3) *With sodium dichromate in acetic acid in presence of sulphuric acid* (compare Wieland, *loc. cit.*). An uncrystallisable brown solid, m. p. above 300°, was obtained.

Reduction of 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl.*—This compound proved exceedingly stable towards reducing agents and also towards reagents known to bring about the dissociation of tetra-arylhydrazines. Boiling with zinc and glacial acetic acid (compare Wieland and Gambarjan, *loc. cit.*), or with the same reagents along with hydrochloric acid (Wieland and Haas, *Ber.*, 1922, **55**, 1804), or with tin and alcoholic–hydrochloric acid failed to effect any reduction. Similarly, the action of metallic sodium in an alcohol–benzene or in amyl-alcoholic solution produced no change.

No dissociation could be effected (*a*) by boiling with 2*N*-sulphuric acid (compare Franzen and Zimmerman, *Ber.*, 1906, **39**, 2566), (*b*) by treating an acetic acid solution with concentrated sulphuric acid, (*c*) by boiling in xylene for 1 hour (compare Wieland, *Annalen*, 1911, **381**, 200; 1912, **392**, 156), (*d*) by passing nitric oxide into a toluene solution of the dicarbazyl derivative at 90° (compare Wieland, *loc. cit.*).

Reduction with hydriodic acid. 3 : 6 : 3′ : 6′-Tetrabromo-9 : 9′-dicarbazyl (0·5 g.) was heated at 150° with concentrated hydriodic acid (3 c.c.) for 5 hours. The reaction mixture was then washed into a solution of sulphur dioxide in water. The white product thus obtained was well washed with water and extracted with boiling absolute alcohol, and the alcoholic extract was treated with animal charcoal and evaporated to dryness. The residue crystallised from benzene in white plates, m. p. 235—239°, identical with carbazole. That part of the reduction products which was insoluble in alcohol (0·03 g.) was shown, after recrystallisation from acetone, to be unchanged 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl.

Synthesis of 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl.*—3 : 6-Dibromocarbazole (1 g.) and finely divided potassium (0·5 g.) were boiled together in pure, dry benzene (25 c.c.) for 1 hour. A yellow powder separated which was possibly the potassium derivative. The mixture was cooled, and iodine (0·6 g.) in dry benzene (10 c.c.) added. After ½ hour, the liquid was filtered, the residue washed with benzene containing a little iodine, and the combined filtrate and washings were evaporated almost to dryness; alcohol was then added. The precipitated solid was extracted three times with boiling alcohol, and the insoluble portion crystallised first from benzene and then from glacial acetic acid, giving white plates, m. p. 249—250°, which were identical with the oxidation product of 3 : 6-dibromocarbazole. Yield 20%. No other products were isolated.

3 : 6-*Di-iodocarbazole* was obtained by Tucker's method (J., 1926, 546). A useful method of purification, which avoids preparation and subsequent hydrolysis of 3 : 6-di-iodo-9-acetylcarbazole, is as follows.

Crude 3 : 6-di-iodocarbazole (1 g.) was dissolved in acetone (20 c.c.), finely powdered potassium permanganate (0·15 g.) added, and the solution boiled for 20 minutes; it was then poured into a solution of sulphur dioxide. The white precipitate, on crystallisation from benzene, gave pure 3 : 6-di-iodocarbazole, m. p. 204—206°. The m. p. of the crude material may thus be raised about 15°.

Oxidation of 3 : 6-*Di-iodocarbazole*.—(1) *With potassium permanganate in acetone.* To a boiling solution of 3 : 6-di-iodocarbazole (2 g.) in a mixture of pure acetone (20 c.c.) and benzene (6 c.c.), a large excess (2—3 g.) of powdered potassium permanganate was added, in 4 portions, during 2 hours. The manganese precipitate was removed and extracted with benzene, the extracts were added to the main filtrate, and the whole was evaporated to dryness. The residue, after being washed with cold acetone, was crystallised from benzene–acetone; small, white cubes of 3 : 6 : 3′ : 6′-*tetraiodo*-9 : 9′-*dicarbazyl*, m. p. 269—270°, were then obtained (Found : I, 60·9; *M*, cryoscopic in benzene, 824. $C_{24}H_{12}N_2I_4$ requires I, 60·8%; *M*, 834). Yield 20%. Much unchanged 3 : 6-di-iodocarbazole was recovered from the acetone washings. 3 : 6 : 3′ : 6′-Tetraiodo-9 : 9′-dicarbazyl closely resembles the tetrabromo-compound. The crystalline form is the same, and the solubilities differ only in being slightly lower for the former.

In the above oxidation, the use of the mixed solvent (acetone–benzene) materially improved the yield of the oxidation product, which was rarely as much as 15% if acetone alone was used (compare Branch and Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 2411).

(2) *With sodium dichromate in glacial acetic acid.* 3 : 6-Di-iodocarbazole (1 g.) was dissolved in glacial acetic acid (80 c.c.), and sodium dichromate (0·5 g.), dissolved in the minimum quantity of water, was added. The solution was boiled for ½ hour. The flocculent precipitate was removed and extracted with alcohol, and the insoluble portion was crystallised, first from benzene–acetone and then from benzene; small, white cubes, m. p. 269—270°, of 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl were thus obtained.

Synthesis of 3 : 6 : 3′ : 6′-*Tetraiodo*-9 : 9′-*dicarbazyl.*—3 : 6-Di-iodocarbazole (1 g.) was added to finely divided potassium (0·3 g.) in pure dry benzene (20 c.c.), and the mixture boiled for 1½ hours. As in the case of 3 : 6-dibromocarbazole, a yellow solid separated. After the mixture had cooled, a solution of iodine (0·5 g.) in dry benzene (10 c.c.) was added with constant shaking. After 1 hour, the liquid was filtered, the residue washed with benzene containing iodine, and the combined filtrate and washings were evaporated to dryness. The solid thus obtained was extracted with alcohol (to remove unchanged 3 : 6-di-iodocarbazole), and the insoluble residue crystallised from benzene (animal charcoal), white cubes, m. p. 269—270°, identical with the oxidation product of 3 : 6-di-iodocarbazole, being deposited.

Reduction of Dicarbazyl A (m. p. 220°).—Dicarbazyl A (0·5 g.) was heated under pressure with concentrated hydriodic acid at 150° for 15 hours. The reaction mixture was washed into water, and the suspension treated with sulphur dioxide to remove free iodine. The separated solid was completely soluble in boiling alcohol, indicating that no dicarbazyl A remained unreduced, since this substance is insoluble in alcohol. The alcoholic solution deposited yellowish needles, which, after one crystallisation from benzene, melted at 235—238° (with sublimation) and were identified with carbazole in the usual way. No other substance could be detected.

Reduction of Dicarbazyl B (m. p. 265°).—The treatment of dicarbazyl B (0·2 g.) with hydriodic acid (3 c.c.) was that described for dicarbazyl A. The product was soluble in alcohol and was a white, non-crystallisable substance, m. p. 100—110°, which has not yet been identified, but is being further investigated.

Reduction of the Amorphous Product C (m. p. 175°).—The substance C (0·5 g.) was heated with concentrated hydriodic acid for 20 hours at 150°. The product of reduction was isolated as in the reduction of dicarbazyls A and B. The major portion of it was soluble in alcohol; the solution deposited small plates, m. p. 235—238°, identical with carbazole. The alcohol-insoluble portion, after repeated extraction with the solvent, melted at 245—260°. It was dissolved in benzene and the solution, after being boiled with animal charcoal for ¼ hour, was filtered into excess of boiling alcohol. The precipitated solid was redissolved in benzene and the foregoing process repeated five or six times; there was then obtained a small amount of a cream-coloured, amorphous substance, m. p. 300—310°, which would not crystallise from any solvent. It is being further investigated.

Bromination of Dicarbazyl A.—It was found essential to use very pure dicarbazyl both in bromination and in iodination. Even an amount of impurity causing a depression of 2—3° in the m. p. of dicarbazyl A makes it almost impossible to purify the product of halogenation.

Dicarbazyl A (0·5 g.) was dissolved in the minimum quantity of boiling glacial acetic acid, a solution (3·5 c.c.) of bromine (1 c.c.) in glacial acetic acid (9 c.c.) gradually added, and the turbid mixture heated on the water-bath for ½ hour; small, white, glistening plates had then separated. After cooling, these were removed, washed with boiling alcohol, and crystallised twice from benzene, small, hard cubes, m. p. 249—250°, identical with synthetic 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl, being obtained.

Iodination of Dicarbazyl A.—(1) To a solution of pure dicarbazyl A (0·5 g.) and finely divided iodine (0·75 g.) in boiling glacial acetic acid (35 c.c.), concentrated nitric acid (2·5 c.c.) in glacial acetic acid (10 c.c.) was added drop by drop until the iodine colour was discharged. After cooling, the precipitated product was removed and washed with sulphur dioxide solution and boiling alcohol. The residue crystallised from benzene in slightly yellow cubes, m. p. 269—270°, and was identical with synthetic 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl. The yellow colour, which was probably due to slight nitration, was not removed by animal charcoal.

(2) To a solution of dicarbazyl A (0·23 g.) in the minimum quantity of glacial acetic acid were successively added powdered potassium iodide (0·36 g.) and, after slight cooling, powdered potassium iodate (0·5 g.). The whole was boiled until the iodine colour had vanished, and was then poured into a solution of sulphur dioxide. The product was 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl.

9 : 9′-*Dicarbazyl.*—We made several attempts to convert 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl, but without success. Solid 9 : 9′-dicarbazyl, or a solution in glacial acetic acid, was unaffected by cold, and sulphonated by hot, concentrated sulphuric acid. Hydrochloric acid or acetic anhydride, heated under pressure with 9 : 9′-dicarbazyl, produced no change.

Many fruitless attempts were also made to synthesise 9 : 9′-dicarbazyl (i) by removal of sulphur from di-*o*-thiotetraphenylhydrazine (Pesci, *Gazzetta*, 1916, **46**, i, 103; compare Gosko, *Ber.*, 1887, **20**, 233), (ii) by the action of halogens on 9-potassiocarbazole. The action of finely divided potassium on carbazole did not give 9-potassiocarbazole as in the case of the halogen derivatives.

Oxidation of 1 : 3 : 6 : 8-*Tetrabromocarbazole.*—Potassium permanganate in acetone would not oxidise this compound.

1 : 3 : 6 : 8-Tetrabromocarbazole (Votoček, *Chem. Ztg.*, 1896, **20**, 190) (1 g.) was dissolved in boiling glacial acetic acid (60 c.c.), and sodium dichromate (0·75 g.) was added. After boiling for 1 hour,

the mixture was poured into water, and the precipitate was separated and extracted with warm acetone. The insoluble residue, after several crystallisations from benzene, gave a minute quantity of small crystals, m. p. above 300°, insoluble in acetone or alcohol and almost so in glacial acetic acid. A sufficient quantity for analysis has not yet been obtained.

Amorphous Substance C, m. p. 175° (Perkin and Tucker, *loc. cit.*). —Analysis of *C* gave C, 86·8; H, 5·1; N, 8·1; *M*, 546. $C_{36}H_{23}N_3$ requires C, 86·9; H, 4·6; N, 8·45%; *M*, 497. Distillation from a paraffin bath at 300° produced carbazole and a residue, which, after purification in a manner similar to that used for the high-melting reduction product of C, was obtained as a cream-coloured solid, m. p. about 320° (Found: C, 86·1, 86·2; H, 4·9, 4·95; N, 8·2, 8·0. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·9; N, 8·4%). No crystalline derivative of this could be obtained, nor any acetyl, methyl or halogen derivative of the amorphous substance C.

The substance C was not produced by prolonged treatment of 9 : 9′-dicarbazyl with potassium permanganate in acetone.

Summary.

(*a*) 3 : 6 : 3′ : 6′-Tetrabromo-9 : 9′-dicarbazyl (m. p. 249—250°) has been prepared by the oxidation of 3 : 6-dibromocarbazole and has been synthesised by the action of iodine on 3 : 6-dibromo-9-potassiocarbazole.

3 : 6 : 3′ : 6′-Tetraiodo-9 : 9′-dicarbazyl has similarly been prepared and synthesised.

(*b*) The dicarbazyl A, m. p. 220°, of Perkin and Tucker (*loc. cit.*), on bromination, gave 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl. It is therefore concluded that dicarbazyl A is 9 : 9′-dicarbazyl.

(*c*) It has not been found possible to convert 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl.

Our thanks are due to the Trustees of the Ferguson Bequest Fund, Glasgow, for a fellowship which enabled one of us (J. McL.) to take part in this research.

UNIVERSITY OF GLASGOW. [*Received, March 9th.* 1927.]

CLXVII.—*A New Scaly Variety of Aluminium Hydroxide.*

By PANCHANAN NEOGI and ANIL KRISHNA MITRA.

ALTHOUGH several varieties of aluminium hydroxide have been described, there is no definite evidence that any of them are crystalline. The gelatinous precipitate obtained by adding ammonia to solutions of aluminium salts was stated by Ramsay (J., 1877, **32**, 395) to be $Al_2O_3,5H_2O$ if air-dried, or Al_2O_3,H_2O if dried at 300° but Allen (*Chem. News*, 1900, **82**, 75) found that the amorphous hydrate had the composition $Al_2O_3,3H_2O$ and was converted into $Al_2O_3,2H_2O$ if heated at 100° or dried over sulphuric acid. Tommasi (*Chem. Zentr.*, 1905, ii, 605) described what he called a δ-modification ($Al_2O_3,3H_2O$), obtained by keeping the ordinary hydroxide under water for several months; this was amorphous and dissolved in acids and alkalis with difficulty. A so-called β-modification (also $Al_2O_3,3H_2O$) has been described by Noyes and Whitney (*Z. physikal. Chem.*, 1894, **15**, 694) and others as being deposited from soluble aluminates; this was regarded as identical with the crystalline mineral gibbsite (Ditte, *Compt. rend.*, 1893, **116**, 183) until Russ (*Z. anorg. Chem.*, 1904, **41**, 216) showed that it was not crystalline.

Whilst reducing various nitrates by means of the aluminium–mercury couple, we met with glistening scales which were shown by careful qualitative tests to be pure aluminium hydroxide. These are stable and have the composition $Al_2O_3,4H_2O$ and d^{31° 1·5490. Under the microscope, they show reflexions from innumerable planes, but no doubly-refracting crystals and no resemblance to gibbsite; in view of the flaky appearance, however, it is probable that the substance consists of isometric crystals. As recrystallisation was impossible, no crystals have been obtained large enough to permit of crystallographic classification.

By the action of the aluminium–mercury couple in water alone, aluminium hydroxide is obtained in a gelatinous condition mixed with black particles (Reichard, *Pharm. Z.*, 1907, **40**, 569), so that it is not justifiable to assign a definite composition to it (compare Cossa, *Z. Chem.*, 1879, **13**, 443).

Certain other nitrates and nitrites, such as those of the alkali metals, give a scaly aluminium hydroxide under the same conditions, but it is often accompanied by a much larger quantity of the gelatinous variety, and barium (and, to a less extent, strontium) nitrate gives the best product.

Besides the nitrates, aqueous solutions of the alkali bromates and iodates were similarly reduced, and the aluminium hydroxide obtained again consisted of a mixture of the gelatinous and scaly varieties, but was usually contaminated with halides.

EXPERIMENTAL.

The freshly-prepared aluminium–mercury couple was added to a concentrated solution of barium nitrate, which covered it to a depth of one or two inches. The reaction commenced at once with the evolution of heat, and the flask was then closed with a soda-lime tube to exclude carbon dioxide and immersed in ice-water. Bright scales of aluminium hydroxide were deposited on the couple, and after a few minutes the supernatant liquid together with the hydroxide was transferred to a large conical flask, which was closed with a cork in order to prevent access of atmospheric carbon dioxide. The couple could be used again with fresh solution and the supernatant liquid in the large flask could be decanted and used again. A quantity of the scales was thus obtained in a few hours; they were repeatedly washed by decantation with large volumes of water until free from barium and any gelatinous variety accompanying it, filtered off, and washed with alcohol and finally with ether. They dried rapidly, retained their lustre in a desiccator, and showed no tendency to absorb water during preparation for analysis, as is the case with the ordinary amorphous variety.

The scales were dissolved in hydrochloric acid and tested for mercury with negative results. (Hasty or negligent washing without repeated decantation leaves traces of barium and mercury.) They were also found to be free from nitrate, nitrite, nitrogen, and peroxidic oxygen.

Ignition of the substance, dried for several days, in a platinum crucible showed a loss of 41·0, 41·2% (Calc. for $Al_2O_3,4H_2O$: 41·4%). Strong ignition in a current of dried air yielded 41·6, 41·0% to calcium chloride tubes, the last molecule of water being removed only with difficulty. Aluminium was estimated after solution in hydrochloric acid (Al_2O_3, found: 59·05, 58·85. Calc.: 58·6%). Loss at 100°, 11·1 (Calc. for $1H_2O$: 9·6%). After the substance had been kept for 3 weeks in a desiccator, its composition, $Al_2O_3,4H_2O$, was unchanged.

The scales were soluble in mineral acids, but insoluble in methylamine, in which the ordinary precipitated hydroxide is soluble (Renz, *Ber.*, 1903, **36**, 2751).

We offer our thanks to Professor S. L. Biswas of the Geological Department of this College for kind assistance in the microscopic examination.

PRESIDENCY COLLEGE, CALCUTTA. [*Received, August 30th,* 1926.]

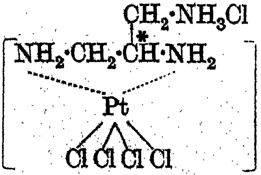
CLXVIII.—*Tetrachloro(triaminopropane-γ-monohydrochloride)platinum, an Optically Active Complex Salt of a New Type.*

By FREDERICK GEORGE MANN.

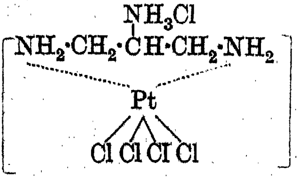
IT has recently been shown by the present author (J., 1926, 2681) that αβγ-triaminopropane, $NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$, co-ordinates with platinum and copper to give two complex salts of novel type, in which only two of the three amino-groups in the triaminopropane molecule are joined to the metal, the third being free for normal salt formation with acids. Quadrivalent platinum thus gives tetrachloro(triaminopropane-monohydrochloride)platinum, $Cl_4Pt,NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl$ (I). Here the metallic complex consists of platinum, of co-ordination number 6, linked to four chlorine atoms and to two of the three amino-groups of the base: it is therefore neutral and non-ionic, being, in its co-ordination linkages, of the same general type as tetrachloroethylenediamineplatinum, $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2]$. Since, however, the third free amino-group, being unco-ordinated and outside the ring, forms a hydrochloride, the compound in solution furnishes one chlorine ion.

Such a compound may exist in two alternative forms. The platinum may either be co-ordinated to the α- and β-amino-groups, leaving the γ-amino-group free to form the monohydrochloride (II), in which case the triamine is acting for co-ordination purposes as a substituted ethylenediamine, or, alternatively, the platinum may be co-ordinated to the α- and γ-amino-groups, leaving the β-amino-group free to form the hydrochloride (III); in this case the triamine is acting as a substituted trimethylenediamine. A possible method of deciding between these two alternative constitutions was at once suggested by the fact that co-ordination through the α- and β-amino-groups (II) causes the carbon atom marked * to become asymmetric, since it is linked on the one hand to a methylene-amino-group ($\cdot NH_2{\cdot}CH_2\cdot$) and on the other to a methylene-ammonium radical ($\cdot CH_2{\cdot}NH_3\cdot$). Such a compound should therefore be capable of resolution into optically active forms.

(II.)



(III.)



Co-ordination through the αγ-diamino-groups (III) gives, however, a symmetrical compound which cannot be so resolved

Attempts were therefore made to resolve this compound by converting the hydrochloride of the free amino-group into the corresponding *d*-camphor-β-sulphonate. The latter compound on fractional recrystallisation from water gave finally l-*tetrachloro*(*triaminopropane-mono*-d-*camphor*-β-*sulphonate*)*platinum*, having $[M]_{5461}^{15^\circ} = -426^\circ$. This compound on treatment with calcium chloride gave the l-*tetrachloro*(*triaminopropane-monohydrochloride*)*platinum* of $[M]_{5461}^{15^\circ} = -502^\circ$. The racemic product was then converted into the *l*-camphor-β-sulphonate, which on recrystallisation furnished similarly d-*tetrachloro*(*triaminopropane-mono*-l-*camphor*-β-*sulphonate*)*platinum*, having $[M]_{5461}^{15^\circ} = +424^\circ$, which was in turn converted into the d-*tetrachloro*(*triaminopropane-monohydrochloride*)*platinum* of $[M]_{5461}^{15^\circ} = +501^\circ$. The two optically active monohydrochlorides differ further from the racemic compound in that they crystallise in the anhydrous form, whilst the racemic compound has one molecule of water, which is not readily removed (Mann, *loc. cit.*).

It follows from these results that the platinum compound has the constitution (II), *i.e.*, that the triaminopropane co-ordinates with platinum more readily through the α- and β-amino-groups to form a five-membered ring compound having an asymmetric element, than through the α- and γ-amino-groups, whereby a six-membered ring compound of high symmetry would have been formed.

It should be emphasised that not only is this platinum compound of entirely novel type, but the cause of its optical activity also is novel. All optically active complex salts hitherto recorded have owed their activity to one (or both) of two factors. Either the complex itself has been dissymmetric, and therefore capable of resolution, *e.g.*, the trisethylenediaminecobaltic complex,

$$[\mathrm{Co(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3}]''',$$

or, alternatively, the complex has contained a constituent dissymmetric molecule which has been resolved before the preparation of the complex salt. Thus *d*-αβ-propylenediamine,

$$\mathrm{NH_2{\cdot}CH_2{\cdot}\overset{*}{C}H(NH_2){\cdot}CH_3},$$

gives a *d*-trispropylenediaminecobaltic complex,

$$[\mathrm{Co\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_3\}_3}]''',$$

the activity of which is due to the active nature of the constituent amine molecules: here, however, the complex also is itself dissymmetric, and a secondary activity can be manifested by the complex as a whole. In the platinum compound under discussion, however, asymmetry of the central (or β) carbon atom is induced by the mode of co-ordination of the triaminopropane molecule and by the consequent orientation of the co-ordination linkages: the asymmetry of this element therefore does not arise until the co-ordination compound itself is formed. This is the first case to be recorded in which the asymmetry of a carbon atom arises from the operation of auxiliary valencies.

Attempts have been made to replace the four co-ordinated chlorine atoms in tetrachloro(triaminopropane-monohydrochloride)-platinum with further basic groups by treating the compound in solution with ammonia and with ethylenediamine. The action of such bases is, however, solely to withdraw the hydrogen chloride from the free amino-group : the latter at once co-ordinates with the platinum, expelling a chlorine atom from the complex, and the insoluble *trichlorotriaminopropaneplatinic monochloride,*

$$[Cl_3PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2]Cl,$$

is thus formed.

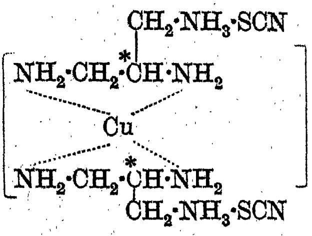
Tetrachloro(triaminopropane-monohydrochloride)platinum gives a characteristic reaction when treated in solution with oxalic acid, since the very slightly soluble *tetrachloro(triaminopropane-hydrogen-oxalate)platinum,* $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,(CO_2H)_2]$, is rapidly precipitated. When this compound is boiled for several hours in aqueous solution, both the unco-ordinated amino-group and the oxalic acid enter the complex, displacing three chlorine atoms, thus furnishing *monochloromonoxalatotriaminopropaneplatinic monochloride,* $[Cl(CO{\cdot}O{\cdot})_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2]Cl$.

It has also been shown (Mann, *loc. cit.*) that copper co-ordinates with triaminopropane to give salts such as *bis(triaminopropane-monothiocyanate)cupric dithiocyanate,*

$$[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_3(SCN)\}_2](SCN)_2 \text{ (IV).}$$

Here the copper atom is linked to two molecules of the base, but, since it has a co-ordination number of 4, to only two amino-groups in each molecule of the triamine. The metal is thus fully co-ordinated, and the complex therefore bivalent; the two unco-ordinated amino-groups, however, as in the platinum compound, are neutralised by normal salt formation, and in solution thus furnish two additional ions. It would follow by analogy that the αβ-diamino-linkage probably obtains also in this copper compound, which

(V.)



would then have the constitution (V), the carbon atoms marked * being asymmetric. Such a compound should exist in racemic, dextro-, lævo-, and *meso*-forms, and if the four co-ordination linkages of the copper are directed to the corners of a regular tetrahedron (Mills and Gotts, J., 1926, 3121), the dextro-, lævo-, and *meso*-forms should each exist in two forms, in which the copper has the *d*- and the *l*-configuration respectively. In view of the intensely deep violet colour of these copper compounds, no attempts at resolution have yet been made.

Further work is now being carried out to determine the mode of co-ordination of triaminopropane with various noble metals, such as iridium and palladium, and with certain bivalent metals such as zinc, cadmium, and mercury, and to determine further whether such compounds are capable of resolution into optically active forms.

The various types of complex salts furnished by triaminopropane may be conveniently summarised here (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **107**, 80; J., 1926, 2675; Mann, J., 1926, 2682):—

1. Metals of co-ordination number 4:

A. Triaminopropane acting as a diamine: Bis(triaminopropane-γ-monothiocyanate)cupric dithiocyanate,

$$[Cu\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_3\cdot SCN\}_2](SCN)_2.$$

B. Triaminopropane acting as a triamine: Tetratriaminopropanetricupric hexathiocyanate,

$$Cu_3\{(NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2)_4\}(SCN)_6.$$

2. Metals of co-ordination number 6:

A. Triaminopropane acting as a diamine: Tetrachloro(triaminopropane-γ-monohydrochloride)platinum,

$$[Cl_4PtNH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_3Cl].$$

B. Triaminopropane acting as a triamine: (*a*) Triacido-triammine type. Trichlorotriaminopropaneplatinic monochloride, $[Cl_3PtNH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2]Cl$. (*b*) Hexammine type. Bistriaminopropanecobaltic trichloride,

$$[Co\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2]Cl_3,$$

and the corresponding nickel and rhodium salts.

EXPERIMENTAL.

All rotations given in this paper have been measured at 15° in a 4-dcm. polarimeter tube, and, unless otherwise stated, are for the mercury green line ($\lambda = 5461$).

Preparation of Tetrachloro(triaminopropane-monohydrochloride)-platinum Monohydrate.—The following quantitative directions supplement the general directions already given (Mann, *loc. cit.*, p. 2686). A solution of triaminopropane trihydrochloride monohydrate (22 g.) in water (200 c.c.) is added to 100 c.c. of a solution of chloroplatinic acid containing 10% of metallic platinum. The clear mixture is boiled under reflux for 3 hours, and the pale yellow solution so obtained twice evaporated to small bulk on the water-bath with intermediate addition of water. The solution is finally concentrated until crystals appear, and on cooling, tetrachloro-(triaminopropane-monohydrochloride)platinum monohydrate rapidly separates (20·3 g.). This material, after two recrystallisations from water, is pure, and darkens at 255—260° and melts at 272—273° (decomp.).

l-*Tetrachloro(triaminopropane-mono-*d-*camphor-*β-*sulphonate)platinum Semihydrate,*

$[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,C_{10}H_{15}O{\cdot}SO_3H],\frac{1}{2}H_2O$.—Hot aqueous solutions of tetrachloro(triaminopropane-monohydrochloride)platinum monohydrate (20 g.) and silver *d*-camphor-β-sulphonate (10·4 g.) were mixed, boiled for 5 minutes, and filtered. The filtrate was evaporated to small bulk on the water-bath, fine, crystalline scales steadily separating; finally the product formed a semi-solid mush, which was at once chilled and filtered. The solid product so obtained was then recrystallised repeatedly from hot water to separate the *l*-base *d*-sulphonate from the more soluble *d*-base *d*-sulphonate. Recrystallisation was best carried out by drying each fraction thoroughly in a vacuum over sulphuric acid, and then adding the powdered product quickly with stirring to a small quantity of almost boiling water. A clear solution was thus rapidly obtained, and on filtering and cooling gave an ample crop of the sulphonate. The latter always retained half a molecule of water of crystallisation even after long exposure to sulphuric acid in a vacuum. After six recrystallisations from water, the *l*-base *d*-sulphonate was obtained as a pale lemon-yellow powder, which in 1·349% aqueous solution had $\alpha = -3{\cdot}44°$, whence $[\alpha] = -63{\cdot}7°$ and $[M] = -426°$: it darkened at 260° and melted to a tar between 270° and 285° (Found: Pt, 29·3. $C_{26}H_{56}O_9N_6Cl_8S_2Pt_2$ requires Pt, 29·25%). This sulphonate does not readily undergo racemisation at the ordinary temperature, since cold aqueous solutions retained their activity unchanged for a week.

A dextrorotatory product also could be separated in the above experiments, for when the cold aqueous mother-liquor from the second fraction was diluted considerably with alcohol and kept over-night, a crop of the camphorsulphonate separated which, in 1·572% solution, had $\alpha = +3{\cdot}08°$, whence $[\alpha] = +49{\cdot}0°$ and $[M] = +323°$. This was thus evidently an optically impure *d*-base *d*-sulphonate, and attempts were made to purify it by repeated dissolution in water and reprecipitation with alcohol. These experiments did not, however, give satisfactory results, and the optically pure dextro-salt was finally obtained by recrystallisation of the *l*-camphorsulphonate, as described below.

l-*Tetrachloro(triaminopropane-monohydrochloride)platinum.*—The sixth fraction of the *l*-tetrachloro(triaminopropane-mono-*d*-camphor-β-sulphonate)platinum, having $[M] = -426°$, was dissolved in a little hot water and the solution was chilled, filtered, and diluted with concentrated aqueous calcium chloride solution. After 4 hours the fine, crystalline monohydrochloride which had separated was collected, well washed with alcohol and ether, and dried. The pure anhydrous l-*monohydrochloride* thus obtained retained its original crystalline form during the processes of filtering and drying; it had evidently, therefore, separated originally in the anhydrous form, and not lost water of crystallisation whilst being dried. It darkened at 260—265° and melted at 277—278° (decomp.) (Found: Pt, 42·2. $C_3H_{12}N_3Cl_5Pt$ requires Pt, 42·2%). A 1·407% aqueous solution had $\alpha^{15°}_{5780} = -5{\cdot}24°$, whence $[\alpha]^{15°}_{5780} = -93{\cdot}1°$, $[M]^{15°}_{578} = -431°$, and $\alpha^{15°}_{5461} = -6{\cdot}10°$, whence $[\alpha]^{15°}_{5461} = -108{\cdot}4°$, $[M]^{15°}_{5461} = -502°$.

Certain observations made in the course of the above work point strongly to the fact that the resolution is successful only if the camphorsulphonate crystallises at a low temperature, and that at higher temperatures it is probably the racemate, or even a product containing an excess of the opposite enantiomorph, which separates. Thus, in the initial preparation, the first crop of crude *d*-camphorsulphonate was obtained by evaporating the solution on the water-bath and then filtering off the solid product which separated. Since the *l*-base *d*-sulphonate is less soluble (in cold water) than the *d*-base *d*-sulphonate, the filtrate from this first crude product should have contained an excess of the *d*-base *d*-sulphonate. Actually it contained an excess of the *l*-base, and when treated with calcium chloride gave a markedly lævorotatory hydrochloride which, in 1·672% aqueous solution, had $\alpha = -0{\cdot}78°$, whence $[\alpha] = -11{\cdot}7°$. When the first crop of crude *d*-camphorsulphonate was subjected to its first recrystallisation, the second fraction obtained now separated after the solution had been chilled; it possessed, of course, an increased lævorotation, and the mother-liquor now contained an excess of the *d*-base, and when treated with calcium chloride gave a feebly dextrorotatory hydrochloride. All the successive fractions also separated after their solutions had been chilled, and the resolution thus proceeded smoothly to completion. It was further observed that if the initial filtrate from the first crop of crude *d*-camphorsulphonate was kept, in the course of 24 hours long, pale lemon-yellow needles of the almost optically pure *l*-base *d*-sulphonate separated, and after several days became contaminated with orange-coloured prisms, presumably those of the *d*-base *d*-sulphonate. In some preparations of the *d*-camphorsulphonate, these long, pale lemon-yellow needles were filtered off before the separation of the orange prisms; they were washed with a little water, and placed over sulphuric acid in a vacuum; they then rapidly lost their crystalline form on partial dehydration, and gave the semihydrate of the almost optically pure *l*-base *d*-sulphonate. Two such samples gave the following rotations respectively: (*a*) a 1·008% aqueous solution had $\alpha = -2{\cdot}53°$, whence $[\alpha] = -62{\cdot}7°$ and $[M] = -419°$; (*b*) a 1·184% solution had $\alpha = -2{\cdot}93°$, $[\alpha] = -61{\cdot}9°$, $[M] = -413°$. These were united and converted into the hydrochloride as before by the action of calcium chloride solution. A crop of the anhydrous and optically pure *l*-hydrochloride was thus obtained (Found: Pt, 42·2%). A 1·328% aqueous solution had $\alpha = -5{\cdot}72°$, $[\alpha] = -108°$, and $[M] = -498°$.

d-*Tetrachloro*(*triaminopropane-mono*-l-*camphor*-β-*sulphonate*)*platinum Semihydrate*.—This was prepared in precisely the same way as the *l*-base *d*-sulphonate, the racemic hydrochloride being treated in solution with silver *l*-camphor-β-sulphonate. The product was recrystallised as before six times from water, and the final crop had in 1·366% aqueous solution, $\alpha = +3{\cdot}47°$, whence $[\alpha] = +63{\cdot}5°$ and $[M] = +424°$ (Found: Pt, 29·15%).

Once again an optically impure crop of the opposite enantiomorph could be obtained by precipitation with alcohol. The filtrate from the second fraction of the *l*-sulphonate, when diluted considerably with alcohol, deposited a crop of the sulphonate which, when separated and dried, had, in 1·218% aqueous solution, $\alpha = -2{\cdot}59°$, whence $[\alpha] = -53{\cdot}1°$ and $[M] = -355°$. No further attempts to complete the resolution of this crop by solution in water and reprecipitation with alcohol were made.

d-*Tetrachloro*(*triaminopropane-monohydrochloride*)*platinum*.—The optically pure, sixth fraction of the *d*-base *l*-sulphonate, having $[M] = +424°$, was treated as before in cold aqueous solution with calcium chloride, and the *d*-tetrachloro(triaminopropane-monohydrochloride)platinum separated in fine crystals, which were filtered off, washed with alcohol and ether, and dried. These crystals, like the *l*-hydrochloride, were anhydrous (Found: Pt, 42·1%), and darkened at 260—265° and melted at 277—278° (decomp.). A 1·555% aqueous solution had $\alpha^{15°}_{5780} = +5{\cdot}80°$, whence $[\alpha]^{15°}_{5780} = +93{\cdot}2°$, $[M]^{15°}_{5780} = +431°$, and $\alpha^{15°}_{5461} = +6{\cdot}73°$, whence $[\alpha]^{15°}_{5461} = +108°$, $[M]^{15°}_{5461} = +501°$.

As before, the initial filtrate from the first crude crop of the *l*-camphorsulphonate slowly deposited a small quantity of the almost optically pure *d*-base *l*-sulphonate in long, pale lemon-yellow needles. These, after being washed and dried, had in 1·232% aqueous solution $\alpha = + 3{\cdot}11°$, whence $[\alpha] = + 63{\cdot}1°$ and $[M] = + 421°$. There was not sufficient of this material, however, for conversion into the *d*-hydrochloride.

*Tetrachloro(triaminopropane-mono-*d*-α-bromocamphor-π-sulphonate)platinum*, $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,C_{10}H_{14}OBr{\cdot}SO_3H]$. —The bromocamphorsulphonate was obtained by mixing hot aqueous solutions of the monohydrochloride (10 g.) and of silver *d*-bromocamphorsulphonate (6·8 g.). The mixed solution, when boiled, filtered, concentrated, and chilled, gave the bromocamphorsulphonate in fine, canary-yellow crystals. These, after being once recrystallised from water and dried, melted at 271—273° (decomp.) (Found: C, 21·0; H, 3·6; Pt, 26·6. $C_{13}H_{26}O_4N_3Cl_4BrSPt$ requires C, 21·15; H, 3·55; Pt, 26·5%). The sulphonate in 1·916% aqueous solution had $\alpha = + 3{\cdot}52°$, $[\alpha] = + 45{\cdot}9°$, and $[M] = + 339°$. This material was now recrystallised three more times from water and, in 1·320% solution, then had $\alpha = + 2{\cdot}48°$, $[\alpha] = + 47{\cdot}0°$, $[M] = + 346°$. Since ammonium *d*-bromocamphor-π-sulphonate has $[M]^{22°}_{5461} = + 347°$ (Pope and Read, J., 1910, **97**, 2201), it was obvious that the activity of the platinum compound was due to the bromocamphorsulphonate ion alone, and that no apparent resolution was being effected.

Trichlorotriaminopropaneplatinic Chloride,
$[Cl_3PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2]Cl$.
—A cold aqueous solution of tetrachloro(triaminopropane-monohydrochloride)platinum was treated with an excess of ammonia solution (*d* 0·966). The fine, yellow, crystalline precipitate which soon appeared was very sparingly soluble in cold water; when boiled with hot water, it slowly dissolved, but the production of a red colour showed considerable reduction to a platinous salt. This ready reduction of co-ordinated platinic to platinous compounds has already been noted by Werner (*Vierteljahrs. Naturfors. Ges. Zurich*, 1917, **62**, 553). The compound was therefore filtered off, and thoroughly washed with cold water, alcohol, and ether, and *trichlorotriaminopropaneplatinic chloride* was thus obtained in fine, yellow crystals which began to darken at about 210° and melted at 242—243° (decomp.) (Found: C, 8·4; H, 2·8; N, 10·1; Pt, 45·9. $C_3H_{11}N_3Cl_4Pt$ requires C, 8·45; H, 2·6; N, 9·9; Pt, 45·8%). The same compound was also obtained when the original monohydrochloride was treated in solution with either one or two molecules of ethylenediamine hydrate.

Tetrachloro(triaminopropane-hydrogen-oxalate)platinum,
$[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,(CO_2H)_2]$.
—This compound rapidly separated when an aqueous solution of the

monohydrochloride was treated with a solution of oxalic acid: it is only slightly soluble in cold water, and when filtered off, washed with water, alcohol, and ether, was obtained as a fine, pale yellow powder, m. p. 248—251° (decomp.) (Found: N, 8·4; Cl, 27·7; Pt, 37·6. $C_5H_{13}O_4N_3Cl_4Pt$ requires N, 8·1; Cl, 27·5; Pt, 37·8%).

Monochloromono-oxalatotriaminopropaneplatinic Chloride,

$$[Cl(CO{\cdot}O)_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2]Cl.$$

—Solutions of tetrachloro(triaminopropane-monohydrochloride)-platinum (9·9 g.) and hydrated oxalic acid (5·2 g.; 2 mols.), each in 125 c.c. of water, were mixed, and the solution was heated to dissolve the precipitated hydrogen oxalate salt. The clear solution was boiled under reflux for 10 hours, and on filtering and cooling deposited fine, yellow crystals. These were twice recrystallised from hot water, in which they were freely soluble, and the *monochloromono-oxalatotriaminopropaneplatinic chloride* was thus obtained as a pale brownish-yellow, microcrystalline powder, which decomposed with foaming between 200° and 210° and was then slowly transformed to a dry, black mass (Found: N, 9·6; Cl, 16·2; Pt, 43·85. $C_5H_{11}O_4N_3Cl_2Pt$ requires N, 9·5; Cl, 16·0; Pt, 44·0%).

Many attempts were made to reduce the monohydrochloride to a compound of bivalent platinum of the type of dichloro(triaminopropane-monohydrochloride)platinum,

$$[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl],$$

a compound which should also have been susceptible to resolution into optically active forms. The yellow monohydrochloride, when treated in hot aqueous solution with sulphur dioxide, slowly underwent reduction with the production of a colourless solution. From this solution various products were obtained, but all on attempted recrystallisation from water underwent decomposition with the evolution of sulphur dioxide, and no well-defined, stable compound could be isolated.

The author is greatly indebted to Professor Sir William Pope, F.R.S., for supplies of platinum and of *l*-camphor, without which this investigation could not have been carried out.

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[*Received, February* 21*st*, 1927.]

CLXIX.—*Sugar Carbonates. Part III. Derivatives of γ-Methylfructoside, γ-Ethylfructoside, and Normal Methylfructoside.*

By Charles Frederick Allpress, Walter Norman Haworth, and John James Inkster.

Since the fructose residue in sucrose is not the normal, but the γ- or labile form, it seems to be a necessary preliminary to the synthesis of sucrose that derivatives of γ-methylfructoside should be made available. The fructoside is readily prepared from ordinary fructose by standard methods, and is characterised by the ease with which its methyl residue can be eliminated. This property induced us to attempt to substitute carbalkyloxy-groups for the hydrogen atoms of the remaining hydroxyls in γ-methylfructoside, and in this we have succeeded. The methods employed are described below, but we have not yet been successful in exposing the reducing hydroxyl group of the substituted ketose. Similar experiments have also been undertaken with *γ-ethylfructoside*.

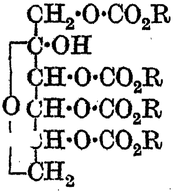
Condensation of γ-methylfructoside with methyl chloroformate in presence of pyridine gave rise to *tetracarbomethoxy γ-methylfructoside*. A series of experiments on the graded hydrolysis of this compound with aqueous-alcoholic solutions containing 0·5% up to 2·5% of hydrogen chloride gave distinct evidence of hydrolysis as indicated by the Fehling's test, and although the methoxyl content of the product (28% OMe) approximated to that (30·1% OMe) required for tetracarbomethoxy γ-fructose, yet the other analytical data showed that the product was not homogeneous. The corresponding *tetracarbethoxy γ-methylfructoside* was also prepared.

Condensation of γ-ethylfructoside with ethyl chloroformate gave *tetracarbethoxy γ-ethylfructoside*, which distilled without difficulty and showed $[\alpha]_D + 27{\cdot}5^\circ$ in ethyl alcohol. The dextrorotatory character of the product would appear to indicate that the γ-ethylfructoside residue has been retained, and indeed the compound gave the usual test with neutral permanganate, which was decolorised instantly. Hydrolysis of the glucosidic ethoxyl residue was not effected completely by heating with 1·25% aqueous hydrogen chloride for 3 hours at 80°, but seemed to proceed with greater ease at 90°, and the product reduced Fehling's solution normally; we have, however, not yet isolated pure tetracarbethoxy γ-fructose. The results of our experiments indicate that the introduction of carbonic ester residues into the γ-fructosides tends considerably to increase the stability of the alkylfructoside residue.

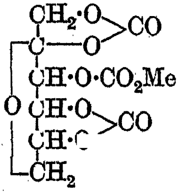
Compounds of the desired type but related to normal fructose have already been described (Allpress and Haworth, J., 1924, **125**, 1228). These are tetracarbomethoxy fructose and tetracarbethoxy fructose, and both these compounds are represented on the basis of the revised structural formula for normal fructose (I). It was previously stated that, although these two crystalline products displayed little, if any, mutarotation in chloroform or acetone, they were probably to be formulated as containing a free reducing group. This conclusion has now been confirmed by the preparation of the corresponding methylfructosides by methylation. These are devoid of action on Fehling's solution, and are recognised as *tetracarbomethoxy methylfructoside* and *tetracarbethoxy methylfructoside*. The carboxylated methylfructosides of the two structural types, the stable and the unstable form, are therefore made available.

In the γ- or unstable series we have not encountered an example of the formation of a true carbonate of the type represented by (II) derived from the normal fructose. The formulation of this crystalline substance, monocarbomethoxy fructose dicarbonate, is, however, now revised on the basis of the new fructose formula (compare Allpress and Haworth, *loc. cit.*).

(I.)



(II.)



EXPERIMENTAL.

Tetracarbomethoxy γ-Methylfructoside.—To a well-cooled mixture of γ-methylfructoside (13 g.; prepared by Menzies' method, J., 1922, **121**, 2238) and dry chloroform containing pyridine (6 mols.), methyl chloroformate was gradually added. The γ-methylfructoside dissolved after agitation for several hours and the reaction was then at an end. Chloroform was removed under diminished pressure, pyridine hydrochloride extracted with water, and the remaining syrup was dissolved in acetone, dried, and distilled after removal of the solvent (b. p. 226—227°/0·1 mm.). Yield, 10—14 g. *Tetracarbomethoxy γ-methylfructoside* was thus obtained as a pale yellow, viscid syrup which showed no tendency to crystallise and did not reduce Fehling's solution. It had $[\alpha]_D + 19·8°$ in acetone ($c = 1·5$) (Found: C, 42·2; H, 5·1; OMe, 33·5; *M*, ebullioscopic in acetone, 415. $C_{15}H_{22}O_{14}$ requires C, 42·3; H, 5·2; OMe, 36·4%; *M*, 426). The compound displayed unexpected stability towards boiling 0·5% aqueous-alcoholic hydrogen chloride; although the product reduced Fehling's solution, it consisted largely of the unaltered fructoside.

Tetracarbethoxy γ-Methylfructoside.—The above procedure being imitated throughout, γ-methylfructoside (3·6 g.) was condensed with ethyl chloroformate, and the product (5·2 g.), consisting of a pale yellow syrup, was twice distilled (yield, 3·8 g.); b. p. 235—238°/0·07 mm., $[\alpha]_D$ + 22·5° in ethyl alcohol. It was devoid of action towards Fehling's solution, but readily reduced cold neutral permanganate (Found: C, 46·8; H, 6·2; OR, 41·9.* $C_{19}H_{30}O_{14}$ requires C, 47·3; H, 6·2; OR,* 43·8%).

This product was submitted to hydrolysis with aqueous-alcoholic hydrogen chloride, and it appeared that with concentrations of acid below 1% no significant change occurred on heating at 80° for 3 hours. Concentrations of acid varying from 1·75% to 2% gave rise to a product which reduced Fehling's solution actively and showed a diminution of rotation to a value which remained constant during several hours.

γ-Ethylfructoside.—Dried ethyl alcohol containing 0·5% of hydrogen chloride was mixed with dried and sieved fructose (1·25 g. for each 100 c.c. of solution), and the solution was observed polarimetrically :

Time (mins.)	0	3	5	7	10	13	18
$[\alpha]_D^{17°}$ ………	−55°	−9·5°	+3°	+10·5°	15·5°	16·5°	17·5°
Time (mins.)	24	27	30	36	47	65	
$[\alpha]_D^{17°}$ ………	17·5°	17·5°	16·5°	16·5°	15·5°	14·5°	

The rotation thus became positive after about 4 minutes, and attained a maximum rotation in 18 to 27 minutes from the time of adding the acid. After this the value slowly decreased, and became negative after several hours.

The following procedure was adopted for the preparation of larger quantities. Fructose (7·5 g.) was shaken with pure ethyl alcohol (500 c.c.) for an hour. Thereafter, alcohol containing hydrogen chloride was added in such quantity as to give a concentration of 0·5% of hydrogen chloride, and this mixture was shaken for 25 minutes, a clear solution being obtained. At this stage the condensation was arrested by neutralising the acid with sodium ethoxide dissolved in dry alcohol. Silver carbonate was then added, which removed the last traces of hydrogen chloride. Filtration and evaporation under diminished pressure yielded a syrup, from which the last traces of alcohol were removed by heating at 80° in a high vacuum. The product, which contained a small quantity of sodium chloride, was extracted four times with boiling ethyl acetate, and the extract yielded on evaporation of the solvent a clear syrup which hardened on cooling. The last traces of solvent were removed by heating for an hour at 100° under 0·05 mm. pressure.

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* OR calculated as 4OEt + 1OMe.

The *γ-ethylfructoside* was readily soluble in water, alcohol, acetone, or pyridine, and showed in alcohol $[\alpha]_D + 28°$. It was devoid of any action towards Fehling's solution except after prolonged boiling, but decolorised neutral permanganate readily (Found: C, 45·7; H, 7·8. $C_8H_{16}O_6$ requires C, 46·2; H, 7·7%).

Tetracarbethoxy γ-Ethylfructoside.—A solution of γ-ethylfructoside (1 mol.) in dry pyridine (7 mols.) was diluted with four times its volume of dry chloroform and cooled to 0°. A chloroform solution of ethyl chloroformate was then added gradually with stirring. After being kept at room temperature for an hour, the solvent was removed under diminished pressure, and the pyridine hydrochloride, which crystallised, was extracted with water. The viscid, yellow residue was dissolved in acetone, reprecipitated by water, and again dissolved in acetone; this solution was dried over magnesium sulphate, and the solvent distilled; the residue, in the absence of traces of pyridine hydrochloride, distilled without difficulty; b. p. 228°/0·05 mm.

The *tetracarbethoxy γ-ethylfructoside* showed in ethyl alcohol, $[\alpha]_D + 27·5°$. It was also soluble in acetone and chloroform. It was not affected by Fehling's solution, but decolorised neutral permanganate (Found: C, 48·3; H, 6·45; OEt, 43·2. $C_{20}H_{32}O_{14}$ requires C, 48·4; H, 6·45; OEt, 45·3%). Towards aqueous-alcoholic hydrogen chloride, this completely substituted derivative of γ-ethylfructoside behaved like the corresponding derivative of γ-methylfructoside, and showed considerable stability even at 100°. Hydrolysis of the glucosidic ethyl group was therefore considerably retarded by the introduction of the carbethoxy-groups.

The Normal Forms of Tetracarbomethoxy Methylfructoside and Tetracarbethoxy Methylfructoside. — *Tetracarbomethoxy methylfructoside* was prepared by subjecting tetracarbomethoxy fructose (m. p. 126°) to two methylations by Purdie's reagents. The isolated product was crystallised from ethyl acetate; it melted at 107° and showed $[\alpha]_D - 126·1°$ in chloroform ($c = 0·6$) (Found: C, 42·3; H, 4·9; OMe, 34·2. $C_{15}H_{22}O_{14}$ requires C, 42·3; H, 5·2; OMe, 36·4%). *Tetracarbethoxy methylfructoside*, prepared by methylating tetracarbethoxy fructose (m. p. 118°) with Purdie's reagents, did not crystallise and showed $[\alpha]_D - 90·9°$ in acetone ($c = 1·2$) (Found: C, 47·1; H, 6·1. $C_{19}H_{30}O_{14}$ requires C, 47·3; H, 6·2%).

The authors are indebted to the Armstrong College Research Fund for financial assistance, which they acknowledge with gratitude.

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[*Received, April 9th*, 1927.]

CLXX.—*The Study of Lactones Derived from Simple Sugars.*

By HARRY DUGALD KEITH DREW, EDWARD HAGUE GOODYEAR, and WALTER NORMAN HAWORTH.

THE investigations of one of us and his collaborators have furnished evidence that the aldoses and ketoses tend to exist normally as amylene oxides, whilst the less stable or γ-forms of sugars appear to be butylene oxides (compare J., 1926, 89, 1858, 2303).

One of the conclusions leading to this fundamental generalisation may be expressed by the statement that the lactones derived from the fully methylated normal sugars are the δ-lactones, whilst the lactones from the γ-forms of these sugars are the more stable γ-lactones; and it has already been shown (*loc. cit.*, p. 89) that a comparison of the relative degrees of stability of the two lactones derived from a given sugar enables each of them to be classified as a γ- or a δ-lactone, and thence reveals the ring structure of each parent sugar form.

The method adopted for comparing the lactones was that of observing the mutarotation–time curves for aqueous solutions, the relative slopes of the curves derived from a pair of lactones enabling each member of the pair to be classified as a γ- or a δ-lactone. When, however, the specific rotations of the free acids in the same solvent are known, a direct comparison of the rate of change of each lactone into the corresponding acid can be made by means of a simple calculation, and the result exhibited in the form of a curve.

This method has the advantage of eliminating the unequal effects due to the rotations of the two methylated acids derived from a pair of lactones; and for this reason we have now determined the specific rotations of a number of acids derived from the γ- and δ-forms of trimethylated pentoses and tetramethylated hexoses, and have plotted the hydration curves of the respective lactones.

In the determination of specific rotation of the acids, a lactone was dissolved in the equivalent of $N/10$-sodium carbonate, and the solution was heated until transformation to the sodium salt was complete. After being cooled, the solution was rapidly neutralised with $N/10$-sulphuric acid and its rotation was then observed at intervals. Extrapolation, where necessary, gave a value for the specific rotation of the pure acid.

The values so obtained are probably not strictly accurate, on account of the presence in the solution of a half-molecular proportion of sodium sulphate, which may modify the rotatory power (compare Clough, J., 1914, **105**, 49; 1915, **107**, 96, 1509). They are considered sufficiently exact, however, to be applicable to the present purpose.

Other effects which cannot easily be allowed for in the observation of mutarotation values of the lactones are the effect of variation of concentration and that of variation in specific rotation of the lactone due to the presence of an increasing proportion of acid. These effects are probably only of a secondary order of magnitude.

With this reservation, then, the percentage of acid present at a given time during the hydration of a lactone is calculable from the expression $100(R - R_l)/(R_a - R_l)$, where R is the specific rotation of the solution at the given time and R_a and R_l are the specific rotations of the lactone in the form of acid and the lactone, respectively. (If r_a represents the true specific rotation of the acid, then $R_a = r_a M_a/M_l$, where M_a and M_l are respectively the molecular weights of acid and lactone.) This expression has also been employed by Levene and Simms (*J. Biol. Chem.*, 1925, **65**, 46).

Table I shows the values of the specific rotations of those lactones which have been studied and of their acids; and the accompanying diagram exhibits in each case the rate of change of lactone to acid in aqueous solution at the ordinary temperature.

TABLE I.

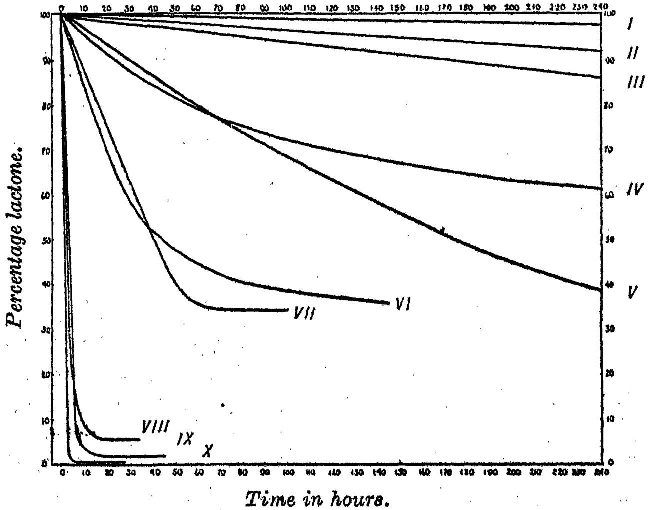
	Specific rotation of lactone (R_l).			Specific rotation of acid (r_a).		
Parent sugar.	$[\alpha]_{5461}$.	$[\alpha]_D$.	Conc.	$[\alpha]_{5461}$.	$[\alpha]_D$.	Conc.
d-2 : 3 : 5 : 6-Tetramethyl glucose ……	+ 72°	+ 63°	1·42	+31·8°	+27·7°	1·08
d-2 : 3 : 4 : 6- „ „	+113	+ 98	1·56	+25·5	+22	1·09
d-2 : 3 : 5 : 6-Tetramethyl galactose ..	− 31	− 27	1·47	− 8·3	− 8·0	0·90
d-2 : 3 : 4 : 6- „ „ ..	+191	+166·5	1·89	+25·5	+22	1·28
d-2 : 3 : 5 : 6-Tetramethyl mannose	+ 78	+ 63	2·51	−27	−23	0·92
d-2 : 3 : 4 : 6- „	+172	+150	1·88	+15·8	+13·7	1·12
l-2 : 3 : 5-Trimethyl xylose ……………	+ 85	+ 74	1·11	+34·4	+29	1·11
l-2 : 3 : 4- „ „ ……………	± 0	± 0	1·87	+29·9	+26	0·98
l-2 : 3 : 5-Trimethyl arabinose …………	− 51	− 44	1·06	− 3·4	− 2·9	0·82
l-2 : 3 : 4- „ „ …………	+206	+180	1·41	+14·6	+13·8	0·72

It will be observed that, in the case of each separate pair of lactones derived from a normal and a γ-form of the same sugar, the curve representing the rate of formation of γ-hydroxy-acid from γ-lactone is sharply distinguished from that representing the rate of formation of the δ-hydroxy-acid from δ-lactone, the latter being much the steeper. These results amply confirm the conclusions arrived at in the former paper (Charlton, Haworth, and Peat, J., 1926, 89). Further, the whole of the curves being taken into consideration, each of the δ-lactone curves is steeper than any γ-lactone curve—a striking fact when the differences in configuration throughout the series are considered.

Between the two extreme types of curve, *viz.*, the very steep δ-lactone curves and the very flat γ-lactone curves, are found two less steep δ-lactone curves (trimethyl δ-xylono- and tetramethyl δ-mannono-lactones) and two less flat γ-lactone curves (trimethyl γ-arabono- and trimethyl γ-glucono-lactones). These modifications in the form of the hydration curves are obviously connected with the configurations of the lactones. Further physico-chemical methods are being brought to bear upon the interpretation of this phenomenon.

Fig. 1.

Comparative rates of hydrolysis of the lactones.



I *Tetramethyl γ-mannonolactone.* II *Tetramethyl γ-galactonolactone.*
III *Trimethyl γ-xylonolactone.* IV *Trimethyl γ-arabonolactone.*
V *Tetramethyl γ-gluconolactone.* VI *Tetramethyl δ-mannonolactone.*
VII *Trimethyl δ-xylonolactone.* VIII *Tetramethyl δ-gluconolactone.*
IX *Tetramethyl δ-galactonolactone.* X *Trimethyl δ-arabonolactone.*

Since the equilibrium values of all the lactones cannot be observed with much accuracy owing to the extreme length of time required in some instances, it is interesting to compare the times in which a quarter (say) of the lactone is changed to acid in the various cases. These are shown in Table II.

Table II.

	γ-Lactones. 25% Acid developed in (hrs.).	δ-Lactones. 25% Acid developed in (hrs.).
Tetramethyl glucono-	75	<1
Tetramethyl galactono-	600	1
Tetramethyl mannono-	(this stage is not reached)	17
Trimethyl xylono-..................	430	22
Trimethyl arabono-	60	<1

The results do not support the generalisation arrived at by Levene and Simms (*loc. cit.*), that the rates of lactone formation among normal hexose acids are practically identical. The speeds of the lactone $\longrightarrow$ acid and acid $\longrightarrow$ lactone reactions are considerably affected by the configuration of the sugar.

Table III shows the approximate proportions of acid and lactone at equilibrium, where these have been measured or calculated from the curves. The ratios of these values give the relative speed constants for the acid $\longrightarrow$ lactone change.

TABLE III.

	γ-Lactones. Acid : lactone at equil.			δ-Lactones. Acid : lactone at equil.		
			Attained in (hrs.).			Attained in (hrs.).
Tetramethyl glucono-	87	13	520	95	5	5
Tetramethyl galactono- ...	—	—	—	98·5	1·5	18
Tetramethyl mannono- ...	11	89	>900	64	36	140
Trimethyl xylono-	31	69	>500	65	35	70
Trimethyl arabono-	45	55	>500	99·5	0·5	4

In many cases (see experimental section), we have re-determined the mutarotation curves of the lactones, using material which is seen, in some instances, to be substantially purer than that hitherto obtained. Thus, three lactones (trimethyl δ-arabono-, tetramethyl δ-mannono-, and tetramethyl γ-glucono-), which were previously known only as syrups, have been obtained in the crystalline condition. In all, six of the ten lactones examined are crystalline. In two of these cases, the specific rotation shows marked enhancement of the former values.

The initial material in the preparation of tetramethyl δ-mannonolactone was pure α-methylmannoside, which was methylated to tetramethyl α-methylmannoside, obtained in a pure crystalline condition. Hydrolysis yielded 2 : 3 : 4 : 6-*tetramethyl mannose*, having $[\alpha]_D^{18°}$ +26° in methyl alcohol ($c = 5{\cdot}15$), rising at equilibrium to +31°. Irvine and Moodie's product (J., 1905, **87**, 1462) had $[\alpha]_D^{20°}$ +14·6° in methyl alcohol ($c = 5$), rising to +17·2° at equilibrium.

Oxidation of tetramethyl mannose gave the crude syrupy lactone, which, after transformation to the *phenylhydrazide*, followed by crystallisation and recovery, gave 2 : 3 : 4 : 6-*tetramethyl mannonolactone* in colourless, prismatic needles (m. p. 23—25°), having $[\alpha]_D^{18°}$ +150° in water ($c = 1{\cdot}88$); and $[\alpha]_D^{23°}$ +130·5°, falling to $[\alpha]_D^{20°}$ +34° in 14 days, in 60% methyl alcohol ($c = 1{\cdot}489$). Irvine and Miss B. M. Paterson (J., 1914, **105**, 915) describe a liquid product having $[\alpha]_D^{20°}$ +78·8°, falling to +38·5° in 10 days, in 60%

methyl alcohol ($c = 1{\cdot}384$), as the above lactone, but quote an inconclusive analytical result for carbon and do not record a value for methoxyl. Their product was obviously impure. The same remark can be applied to the syrup obtained by Levene and Meyer (*J. Biol. Chem.*, 1924, **60**, 167), which had $[\alpha]_D$ +105° in water ($c = 2{\cdot}85$) and gave poor analytical values.

We have repeated the preparation of the 2 : 3 : 5 : 6-tetramethyl mannonolactone described by Levene and Simms (*loc. cit.*), who record an inconclusive analysis; and have found that another product accompanies the lactone under the experimental conditions employed by these authors. The homogeneity of this lactone is therefore under suspicion, and test experiments are in progress to decide the point. In the meantime, the figures recorded in this paper should be regarded as provisional in the case of this lactone and also of the trimethyl γ-xylonolactone. It seems doubtful whether a pure specimen of a completely methylated lactone is readily obtainable by direct methylation of the lactone of a hexonic or pentonic acid. Pure specimens we have handled have been prepared by oxidation of a methylated sugar.

In the case of arabinose, the observations were conducted on the crystalline 2 : 3 : 4-trimethyl δ-arabonolactone (m. p. 45°) isolated as described by Drew and Haworth (this vol., p. 778).

2 : 3 : 5 : 6-Tetramethyl γ-gluconolactone was similarly obtained as a crystalline solid (m. p. 26—27°), having $[\alpha]_D^{21°}$ +62·5° in water ($c = 1{\cdot}415$), a value which substantially agrees with that recorded by Charlton, Haworth, and Peat (*loc. cit.*), *viz.*, $[\alpha]_D$ +61·5°.

In a further paper (*J. Biol. Chem.*, 1926, **68**, 737), Levene and Simms record for tetramethyl δ-gluconolactone a specific rotation of $[\alpha]_D^{22°}$ +108° in water, and for the corresponding equilibrium solution a specific rotation of $[\alpha]_D^{22°}$ +46°; whereas Charlton, Haworth, and Peat (*loc. cit.*) record values of $[\alpha]_D$ +101° and $[\alpha]_D$ +25·6°, respectively. We have now examined two separately prepared specimens of this lactone, and have obtained specific rotations of $[\alpha]_D^{19°}$ +98° for the lactone in water and $[\alpha]_D^{19°}$ +28° for the equilibrium solution. The specific rotation of the acid in water was observed to be $[\alpha]_D^{19°}$ +22° ($c = 1{\cdot}09$) and $[\alpha]_D^{20°}$ +28° ($c = 0{\cdot}9$) for the two samples, as against Levene and Simms's value of $[\alpha]_D$ +40·5°. It is therefore considered that the figure obtained by Levene and Simms is of doubtful accuracy.

EXPERIMENTAL.

Tetramethyl γ-Gluconolactone.—Tetramethyl γ-glucose, oxidised at 75° by means of bromine, gave the *lactone* as an oil ($n_D^{14°}$ 1·4501) which solidified in colourless needles, m. p. 26—27° (Found: C, 51·0; H, 7·6. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%).

In water (c = 1·415), the following rotations were observed:

Time (hrs.).	$[\alpha]^{20°}_{5461}$.	% Lactone present.	Time (hrs.).	$[\alpha]^{20°}_{5461}$.	% Lactone present.
0	+72°	100	240	+48·8°	38·7
73·7	62·3	76	360	42·4	21·8
121·2	58·3	63·7	408	40·7	17·4
144	55·9	57·4	501	38·8	12·4
192	51·6	46			(constant)

For the lactone: $[\alpha]^{21°}_{5461}$ +72°, $[\alpha]^{21°}_{5780}$ +65°, $[\alpha]^{21°}_{D}$ +62·5°. For the acid (calculated as lactone): $[\alpha]^{20°}_{5461}$ +34°, $[\alpha]^{20°}_{D}$ +30° (in water, c = 1·08), rising after 4 days to $[\alpha]^{19°}_{5461}$ +41°.

Tetramethyl δ-Gluconolactone.—In water (c = 1·564), the lactone gave the rotations:

Time (hrs.).	$[\alpha]^{19°}_{5461}$.	% Lactone present.	Time (hrs.).	$[\alpha]^{19°}_{5461}$.	% Lactone present.
0	+112·5°	100	0·58	+95°	79·4
0·12	109	95·9	0·68	91·5	75·3
0·25	105	91·2	1·33	73	53·6
0·33	101·5	86·5	1·82	59	37·1
0·45	100	85·3	16·75	32	5·4 (constant)

For the acid (calculated as lactone): $[\alpha]^{19°}_{5461}$ +27·4° in water (c = 1·095), rising after 6 days to $[\alpha]^{19°}_{5461}$ +33·8°.

Tetramethyl γ-Galactonolactone.—For this lactone, Haworth, Ruell, and Westgarth (*loc. cit.*) give $[\alpha]_D$ −27° for the initial value in water (c = 1·47), changing after 12 days to $[\alpha]_D$ −25°. Thus, 89·7% of lactone is still present after 12 days, the acid (calculated as lactone) having $[\alpha]^{16°}_{D}$ −8·6° in water (c = 0·896). It seems improbable, therefore, that equilibrium had been attained in the period indicated. Further experiments in this connexion are in progress.

Tetramethyl δ-Galactonolactone.—The following values were observed for the lactone in water (c = 1·891):

Time (hrs.).	$[\alpha]^{21°}_{D}$.	% Lactone present.	Time (hrs.).	$[\alpha]^{21°}_{D}$.	% Lactone present.
0	+166·5°	100	3·0	+69·5°	32·0
1·5	114·5	63·5	4·25	47·8	16·8
2·5	84·7	42·7	21·0	26·2	1·7 (constant)

For the acid (calculated as lactone): $[\alpha]^{21°}_{D}$ +24° in water (c = 1·228), rising after 48 hours to $[\alpha]^{21°}_{D}$ +26·3° (compare Haworth, Ruell, and Westgarth, J., 1924, **125**, 2473; Pryde, Hirst, and Humphreys, J., 1925, **127**, 355.

Tetramethyl γ-Mannonolactone.—A sample of the lactone (m. p.

106—107°), prepared by Levene and Simms's process (*loc. cit.*), gave an initial rotation of $[\alpha]_D^{19°}$ +63° in water ($c = 2·51$), falling during 9 days to $[\alpha]_D^{20°}$ +61°. Catalysis with hydrochloric acid gave an equilibrium rotation of $[\alpha]_D^{20°}$ +53°. For the acid, in water ($c = 0·923$): $[\alpha]_D^{21°}$ −23°, becoming $[\alpha]_D^{21°}$ −17° after 5 days. It is clear, therefore, that the mutarotation of the lactone is extremely slow. Further work is in progress to test the purity of the lactone and to determine the equilibrium composition of the aqueous solution.

2 : 3 : 4 : 6-*Tetramethyl* δ-*Mannonolactone.*—Pure α-methylmannoside was methylated by means of sodium hydroxide and methyl sulphate, and then by means of silver oxide and methyl iodide. The product (b. p. 105°/0·03 mm.; $n_D^{16°}$ 1·4494) solidified in crystals of tetramethyl α-methylmannoside, m. p. 38—40°. The mannoside was hydrolysed by 5% hydrochloric acid to 2 : 3 : 4 : 6-*tetramethyl mannose*, obtained as a colourless syrup (b. p. 114·5°/0·035 mm.; $n_D^{19°}$ 1·4597). The overall yield of pure product was 50% (Found: OMe, 50·5. $C_{10}H_{20}O_6$ requires OMe, 52·5%). The sugar had $[\alpha]_D^{18°}$ +26° in methyl alcohol ($c = 5·15$), rising to +31° at equilibrium.

The tetramethyl mannose, on oxidation at 45° with bromine, yielded the crude lactone as a colourless syrup (b. p. 117°/0·04 mm.; $n_D^{17°}$ 1·4643; $[\alpha]_{5461}^{19°}$ +156° in water). Since the analytical figures (C, 50·7; H, 7·8; OMe, 48·8, 49·3%) indicated the presence of appreciable impurity, the whole was converted into the *phenylhydrazide*, white, nacreous flakes from benzene; m. p. 184—185° (Found: C, 56·0; H, 7·6; N, 8·4; OMe, 35·0. $C_{16}H_{26}O_6N_2$ requires C, 56·1; H, 7·6; N, 8·2; OMe, 36·3%). The recrystallised phenylhydrazide was hydrolysed by means of 1% hydrochloric acid, and the *lactone* recovered as a syrup (b. p. 104°/0·02 mm.; $n_D^{16°}$ 1·4650), which solidified in colourless, prismatic needles, m. p. 23—25° after being drained on porous tile in a vacuum (Found: C, 51·2; H, 7·8; OMe, 50·5. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7; OMe, 53·0%).

In water ($c = 1·88$) the following rotations were observed:

Time (hrs.).	$[\alpha]_{5461}^{19°}$.	% Lactone present.	Time (hrs.).	$[\alpha]_{5461}^{19°}$.	% Lactone present.
0	+172°	100	34·3	+102°	54·8
0·3	171	99·4	57·1	88	45·8
5·8	157·5	90·6	71·1	82·5	42·3
9·3	148	84·5	146·3	73·4	36·0 (constant)

For the lactone: $[\alpha]_{5461}^{18°}$ +172·3°, $[\alpha]_{5780}^{18°}$ +153°, $[\alpha]_D^{18°}$ +150°. For the acid (calculated as lactone): $[\alpha]_{5461}^{14°}$ +17°, $[\alpha]_D^{14°}$ +14·8 in water ($c = 1·12$), rising after 88 hours to $[\alpha]_{5461}^{18°}$ +60·7°.

Trimethyl γ-Xylonolactone.—The records of Haworth and Westgarth (J., 1926, 886) give the following mutarotation figures for the lactone in water ($c = 1{\cdot}106$) : *

Time (hrs.)	0	64	168	504
$[\alpha]_D$	+74°	+71·8°	+69·6°	+61·4°
% Lactone present	100	94·6	89·4	70·0

For the acid (calculated as lactone), we observed $[\alpha]_D^{16^\circ}$ +31·7° in water ($c = 0{\cdot}944$), rising after 17 hours to $[\alpha]_D^{16^\circ}$ +33·5° (equilibrium not attained).

Trimethyl δ-Xylonolactone.—Pure trimethyl methylxyloside (m. p. 46—48°) was hydrolysed by means of 3% hydrobromic acid, and the resulting sugar oxidised at 75° with bromine. The lactone (b. p. 101°/0·04 mm.) at once solidified. It crystallised from petroleum in long, colourless needles, m. p. 56° [Found : C, 50·75; H, 7·2; OMe, 48·9; *M*, ebullioscopic in benzene, 200 ($c = 0{\cdot}93$). $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 48·9%; *M*, 190] (compare Haworth and Westgarth, *loc. cit.*). In water ($c = 1{\cdot}871$) the lactone gave :

Time (hrs.).	$[\alpha]_{5461}^{20^\circ}$.	% Lactone present.	Time (hrs.).	$[\alpha]_{5461}^{20^\circ}$.	% Lactone present.
0	± 0°	100	32·75	+13·3°	59·1
6·75	+ 2·4	92·7	46·75	17·4	46·8
22·25	8·8	73·1	70·75	21·4	34·6 (constant)

For the acid (calculated as lactone): $[\alpha]_{5461}^{16^\circ}$ +32·7° in water ($c = 0{\cdot}977$), falling after 8 hours to $[\alpha]_{5461}^{15^\circ}$ +21·5°.

2 : 3 : 5-*Trimethyl γ-Arabonolactone.*—The following values are taken from the record of Haworth and Nicholson (J., 1926, 1902).

Time (hrs.).	$[\alpha]_D$.	% Lactone present.	Time (hrs.).	$[\alpha]_D$.	% Lactone present.
0	−44·4°	100	168	−30·0°	65·0
2	43·8	98·5	288	27·0	57·8
24	40·0	89·3	480	25·2	53·4
120	32·1	70·1			

For the acid (calculated as lactone), we observed $[\alpha]_D^{16^\circ}$ −3°, rising after 40 hours to $[\alpha]_D^{15^\circ}$ −15° (equilibrium not attained).

2 : 3 : 4-*Trimethyl δ-Arabonolactone.*—This was prepared as described by Drew and Haworth (this vol., p. 778). The crystals (m. p. 45°), which were drained on porous tile in a vacuum, could not be recrystallised owing to the remarkable tendency of the

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* This lactone has now been prepared from a different source and identified through the crystalline phenylhydrazide. This specimen gives rather higher mutarotation figures. The result is to increase slightly the declination of the curve for this lactone in Fig. 1, but its relative position in the sequence of the curves is not affected.

substance to absorb water (Found: C, 50·7; H, 7·3; OMe, 45·5. Calc. for $C_8H_{14}O_5$: C, 50·5; H, 7·4; OMe, 48·9%).

For the lactone in water ($c = 1·411$), the following values were observed:

Time (hrs.).	$[\alpha]^{20°}_{5461}$.	% Lactone present.	Time (hrs.).	$[\alpha]^{20°}_{5461}$.	% Lactone present.
0	+206°	100	2·0	+70°	28·4
0·07	199	96·3	2·5	45	15·3
0·5	161	76·3	3·2	21	2·6
1·4	104	46·3	3·8	17	0·5 (constant)

For the lactone: $[\alpha]^{21°}_{5461}$ +206·3°, $[\alpha]^{21°}_{5780}$ +183·5°, $[\alpha]^{21°}_{D}$ +179·5° in water ($c = 1·411$). For the acid (calculated as lactone): $[\alpha]^{19°}_{5461}$ +16° in water ($c = 0·72$), rising after 2 days to $[\alpha]^{21°}_{5461}$ +18° (compare Pryde, Hirst, and Humphreys, J., 1925, **127**, 355).

The authors express their thanks to the Department of Scientific and Industrial Research for a grant and to Messrs J. Avery, B.Sc., W. Charlton, B.Sc., D. I. Jones, B.Sc., and E. J. Miller, B.Sc., for assistance in the laborious preparation of some of the initial materials required in this work.

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[*Received, April 9th*, 1927.]

CLXXI.—*The Nature of the Alternating Effect in Carbon Chains. Part XIX. The Mechanism of Certain Aromatic Migrations.*

By Christopher Kelk Ingold, Ernest Walter Smith, and Charles Cyril Norrey Vass.

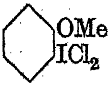
In explanation of the process of halogenation, Fry, Cofman, Francis, and others have supposed that the halogen molecule ionises, the positive ion being the active agent. Whilst, however, it seems unlikely that such a decomposition, involving the exclusive appropriation of electrons by one atom, would take place without external excitation, the electron repulsion of a negative centre (*e.g.*, in an aromatic nucleus) might supply the necessary stimulus by tending to divest a halogen atom of its shared electrons during combination, leaving the other halogen atom to escape as a negative ion. Thus, the activity of a molecular chlorinating agent, X·Cl, should increase with the electron affinity of X, and similarly for bromination and iodination, which agrees with the fact that bromine chloride is a powerful brominating agent, but does not chlorinate, that iodine monochloride iodinates, and, generally, that the efficiency of halogenating agents is in the anticipated order (electron affinity sequence: $Cl > Br > I > OH$):

$Cl{\cdot}Cl > OH{\cdot}Cl$	$Cl{\cdot}Br > Br{\cdot}Br > OH{\cdot}Br$	$Cl{\cdot}I > I{\cdot}I$
(chlorinating agents)	(brominating agents)	(iodinating agents)

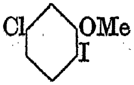
On the other hand, iodine trichloride is a chlorinating agent, but this is explicable on the theory of " singlet " linkings (Prideaux, *Chem. and Ind.*, 1923, **42**, 672; Ingold and Ingold, J., 1926, 1314; Sugden, this vol., p. 1174), since the *positively charged* iodine atom will attract electrons very strongly.

Reasoning on these lines, we deduced, for instance, that the " rearrangements " of aryl iodide dichlorides are not true internal migrations, but substitutions in one aromatic molecule of chlorine derived from another, the process being regenerative and continuous (compare Ingold and Ingold, *loc. cit.*). From this it follows that the ortho–para-migration law need not necessarily be obeyed, and that ordinary orientation rules should hold. A search of the literature revealed much that is consistent with this view [including the important observation by Brazier and McCombie that *p*-iodophenol dichloride, in which the *p*-position is blocked, yields 2-chloro-4-iodophenol (J., 1912, **101**, 968)], and nothing inconsistent with it, except the following.

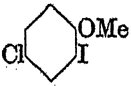
o-Iodoanisole dichloride (I) was prepared by Jannasch and Hinterskirch (*Ber.*, 1898, **31**, 1710), who diagnosed the main product of its decomposition as 5-chloro-2-iodoanisole (II) (para-migration). According to the above mechanism, this would mean that iodine is more strongly *op*-orienting than methoxyl, which is contrary both to the theoretical sequence of these groups and to the order indicated by nitration experiments (Reverdin, *Ber.*, 1896, **29**, 997). The case, in fact, is one in which a meta-" migration " would be anticipated, and, actually, an independent synthesis (*vide* experimental portion) of 4-chloro-2-iodoanisole (III) has shown that this is the real structure of Jannasch and Hinterskirch's product.



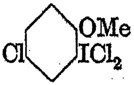
(I.)



(II.)



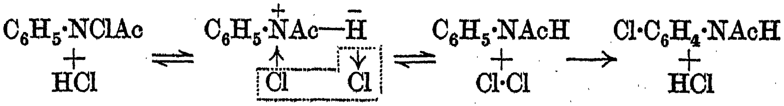
(III.)



(IV.)

The group ·NHAc is more strongly *op*-orienting even than ·OMe (Ingold and Ingold, *loc. cit.*), and collateral evidence of the intermolecular character of these " migrations " was obtained by allowing the dichloride (IV) to decompose in the presence of acetanilide; the latter then acted as an acceptor for chlorine, the products being *p*-chloroacetanilide and chloroiodoanisole (III).

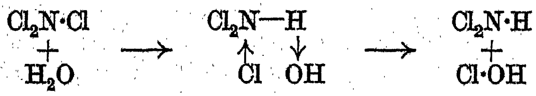
A somewhat similar transference of chlorine to a "foreign" aromatic nucleus has been established by Orton and King (J., 1911, 99, 1185) for *N*-chloro-anilides in the presence of hydrogen chloride, which Armstrong (J., 1900, 77, 1051) proved to be necessary for the conversion of the *N*-chloro-compounds into their *p*-chloro-isomerides. The corresponding explanation, which involves the addition of hydrogen chloride, through hydrogen, to the unshared nitrogen electrons,



$$\begin{array}{c} C_6H_5{\cdot}NClAc \\ + \\ HCl \end{array} \rightleftharpoons \begin{array}{c} C_6H_5{\cdot}\overset{+}{N}Ac—\overset{-}{H} \\ \uparrow \qquad \downarrow \\ \boxed{Cl \qquad Cl} \end{array} \rightleftharpoons \begin{array}{c} C_6H_5{\cdot}NAcH \\ + \\ Cl{\cdot}Cl \end{array} \longrightarrow \begin{array}{c} Cl{\cdot}C_6H_4{\cdot}NAcH \\ + \\ HCl \end{array}$$

(small concentration)

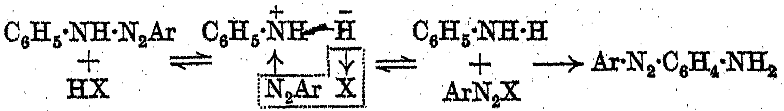
incorporates all the essential features of Orton's theory and one feature of Armstrong's (compare *Brit. Assoc. Reports*, 1910, 85), and is consistent with the equilibrium established by Orton and Jones (J., 1909, 95, 1456) and with the available dynamical data (Blanksma, Orton). It corresponds closely with Sidgwick's explanation of the hydrolysis of halides in its application to nitrogen halides (J., 1924, 125, 2672),



$$\begin{array}{c} Cl_2N{\cdot}Cl \\ + \\ H_2O \end{array} \longrightarrow \begin{array}{c} Cl_2N—H \\ \uparrow \quad \downarrow \\ Cl \quad OH \end{array} \longrightarrow \begin{array}{c} Cl_2N{\cdot}H \\ + \\ Cl{\cdot}OH \end{array}$$

and shows how the lability of the halogen depends on the distribution of charges in the ammonium complex.

The "rearrangement" of aromatic diazoamino-compounds may be similarly regarded, the final irreversible reaction being a diazo-coupling:



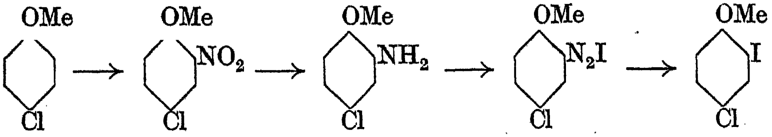
$$\begin{array}{c} C_6H_5{\cdot}NH{\cdot}N_2Ar \\ + \\ HX \end{array} \rightleftharpoons \begin{array}{c} C_6H_5{\cdot}\overset{+}{N}H—\overset{-}{H} \\ \uparrow \qquad \downarrow \\ \boxed{N_2Ar \quad X} \end{array} \rightleftharpoons \begin{array}{c} C_6H_5{\cdot}NH{\cdot}H \\ + \\ ArN_2X \end{array} \longrightarrow Ar{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$$

(small concentration)

This scheme is also in agreement with dynamical observations (Goldschmidt), and here again the transference of the ArN_2-group to a foreign nucleus has been realised (Nietzki, *Ber.*, 1877, 10, 662). Other aromatic migrations may differ in certain respects from the above (see p. 1249), but a circumstance common to them all may be assumed to be the withdrawal of electrons from the mobile group by the attraction of a positively charged atom (compare Orton, *Proc. Roy. Soc.*, 1903, 71, 156).

EXPERIMENTAL.

Preparation of 4-Chloro-2-iodoanisole.—This was obtained from *p*-chlorophenol as follows:



p-Chloroanisole (b. p. 194—198° uncorr.; recorded b. p. 198—202° corr.), obtained by methylation of *p*-chlorophenol with methyl sulphate and 10% sodium hydroxide, was nitrated with cooling and constant stirring in acetic anhydride solution, 5% more than the theoretical quantity of nitric acid (*d* 1·5), previously dissolved in the same solvent, being used. Water was added, and after decomposition of the acetic anhydride the nitro-compound was collected, and washed with dilute sodium hydroxide solution to remove the colour, and with water. The yield was 93% (m. p. 96—97·5°; recorded m. p. 97·5°). Reduction was effected by means of stannous chloride in hot hydrochloric acid, and the 4-chloro-*o*-anisidine (yield 95%, m. p. 82°) isolated by prolonged distillation in steam after addition of a large excess of concentrated sodium hydroxide solution. The base was diazotised in dilute hydrochloric acid below 5°, and the solution was treated with an excess of potassium iodide and warmed until the evolution of nitrogen ceased. The product was distilled in steam, the distillate extracted with ether, and the extract washed successively with hydrochloric acid, sodium hydroxide solution, and water. The residue obtained after drying and evaporation of the ether readily solidified, and crystallised from ligroin in large, transparent, rhomboidal plates, m. p. 48° (Found: C, 31·1; H, 2·1. C_7H_6OClI requires C, 31·3; H, 2·2%).

Chlorination of o-*Iodoanisole.*—Jannasch and Hinterskirch's *o*-iodoanisole dichloride was obtained without difficulty when a chloroform solution (50 c.c.) of *o*-iodoanisole (10 g.) was saturated with dry chlorine. A bright yellow solid separated, which was collected and washed with chloroform; it then melted at about 63° (decomp.). Hydrogen chloride was evolved in the cold, and the main product, contaminated with a pink oil, consisted of the characteristic rhomboidal plates, m. p. 48° (Found: C, 31·3; H. 2·1%), identical with those described above (mixed m. p. 48°).*

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* In Beilstein's "Handbuch" (4te Aufl., Bd. VI, s. 209) the oil, b. p. 273—278°, described by Jannasch and Naphtali (*Ber.*, 1898, **31**, 1715) as the product of decomposition of *o*-iodophenetole dichloride, is referred to as "5-chloro-2-iodophenetole," evidently by analogy with Jannasch and Hinterskirch's "5-chloro-2-iodoanisole." The revision in the orientation of the latter involves a corresponding change in the formula of its homologue.

Dichlorination of o-*Iodoanisole*.—During an attempted preparation of *o*-iodoanisole dichloride, evolution of hydrogen chloride set in, and an iodo-dichloride was obtained probably identical with that described below. This in course of time decomposed, giving a green liquid, from which, by cooling, needles, m. p. 37°, of apparently a *dichloroiodoanisole* were obtained (Found: C, 27·9; H, 2·0. $C_7H_5OCl_2I$ requires C, 27·7; H, 1·65%).

Chlorination of 4-*Chloro*-2-*iodoanisole*.—The iodo-dichloride, which was prepared by means of chloroform in the usual way, has a deeper yellow colour than that derived from *o*-iodoanisole, and melts at about 76° (decomp.). The product of its spontaneous decomposition in chloroform solution was a brown oil, from which, by cooling, crystals of the compound, m. p. 37°, and of 4-chloro-2-iodoanisole (m. p. 48°) were obtained.

Chlorination of Acetanilide by an Aryl Iodide Dichloride.—The dichloride (4 g.) of 4-chloro-2-iodoanisole and acetanilide (1·4 g.) were together dissolved in chloroform. Heat was spontaneously generated, hydrogen chloride was evolved, and the yellow colour of the iodo-dichloride quickly disappeared. The product obtained on concentration of the chloroform solution was distilled in steam, and the residue crystallised from hot water; 1·4 g. (80%) of almost pure *p*-chloroacetanilide were then obtained (m. p. 171—174°; m. p. when fully purified, 175°). The distillate, which contained a liquid and a solid besides the aqueous layer, was filtered; the solid melted at about 60° and appeared to be impure *o*-chloroacetanilide. The non-aqueous liquid, which contained a little chloroform, when separated, dried, and left in a vacuum, completely solidified, yielding nearly pure 4-chloro-2-iodoanisole (m. p. 40—45° unpurified), which was identified, after purification, by direct comparison.

Other Rearrangements.—Numerous experiments, which need not be described in detail, have been made (and are being continued) in order to ascertain whether the hydroxyl group in β-arylhydroxylamines and the arylimino-group in αβ-diarylhydrazines can be transferred to a foreign nucleus by allowing the rearrangement with acids to occur in the presence of another strongly orienting aromatic compound (arylamines and their derivatives, and phenols in solutions of different hydrogen-ion concentration have been used); and whether migrations, directed by an independent substituent, to the meta-position of the same nucleus can be realised. The results have so far been wholly negative, and although we find it difficult entirely to convince ourselves on the grounds of such observations, the conclusion seems to be that the rearrangements of arylhydroxylamines and the benzidine and semidine conversions are not intermolecular processes in the same sense as are the reactions discussed in the introduction to this paper. We are studying along similar lines the migration of nitroxyl and alkyl groups from a side chain to the aromatic nucleus.

THE UNIVERSITY, LEEDS. [*Received, April 23rd*, 1927.]

CLXXII.—*The Alleged Second Isoelectric Point of Gelatin.*

By BHUPENDRA NATH GHOSH.

THE observation of a minimum in the viscosity curve of gelatin at p_H 7·7 at 40° by Davis and Oakes (*J. Amer. Chem. Soc.*, 1922, **44**, 464) and of a similar minimum in swelling by Wilson and Kern (*ibid.*, p. 3633; 1923, **45**, 3139) led to the suggestion that gelatin has a second isoelectric point at this p_H. This was further supported by Matthews (*ibid.*, 1924, **46**, 852), who noticed two minima in the ultra-violet absorption spectrum of gelatin at p_H 4·7 and p_H 7·65, corresponding to the two isoelectric points. Wilson and Kern tried to explain these properties by assuming that gelatin can exist in two forms, the "gel" and the "sol" form, the former having an isoelectric point at p_H 4·7 and the latter at p_H 7·7. Increase of temperature or of p_H can transform the "gel" form to the "sol" form. Kraemer (*J. Physical Chem.*, 1925, **29**, 411) and Kraemer and Fanselow (*ibid.*, p. 1169) have further investigated the subject. They have discussed the different views regarding the existence of the two forms of gelatin, *i.e.*, the "sol" and "gel" forms of Wilson and Kern, and the keto-enol transformation suggested by Lloyd (*Biochem. J.*, 1920, **14**, 147), and have concluded that such assumptions are not justifiable and do not lead to useful results. They believe that the properties of gelatin can in many respects be explained from our knowledge of the behaviour of such colloids as ferric hydroxide sol. In Kraemer's opinion, the second isoelectric point at p_H 7·7 corresponds with the neutralisation of the negative charge of gelatin by positive ions in the alkaline solution.

Bogue (*J. Amer. Chem. Soc.*, 1925, **47**, 1194) has recently measured the optical rotation of gelatin sol at different hydrogen-ion concentrations, and concludes that gelatin has no second isoelectric point at p_H 7·7. In view of these controversies, it seemed desirable to measure the electrical charge of gelatin over a range of hydrogen-ion concentrations covering the two isoelectric points. The electro-endosmotic method of measurement has been chosen as being very suitable for measuring the charge of colloidal gels. Moreover, this method gives an idea of the resultant charge per unit area of the surface, and hence, even if gelatin contains particles having opposite charges, then, assuming that the amount of charge carried by each particle is the same, the rate of flow of water gives an indication as to which type of particle is in excess.

EXPERIMENTAL.

The gelatin used was purified by repeated washing with dilute acetic acid solution as suggested by Loeb (*J. Gen. Physiol.*, 1918, **1**, 45). The purified sample was dehydrated by washing it with absolute alcohol and then dried in air. Its ash content was 0·23%. 1·5 G. of the substance were placed in a Pyrex glass bottle containing 300 c.c. of a dilute sodium hydroxide and phosphoric acid mixture at 20° and left in contact with the solution for 24 hours. The p_H of the solution in equilibrium with the substance was determined by comparison with a set of standards as recommended by Clark and Lubs. The swollen masses of gelatin were then transferred to a U-tube, melted by warming in a water-bath, and then allowed to set at 18° for nearly 4 hours. The U-tube was then filled with the solution with which the jelly had previously been left in contact. The other experimental arrangements were exactly the same as described by the author in a previous paper (J., 1926, 2609). The experiments were carried out at 18° and the results are given in Table I, in which *b* represents the distance (in cm.) moved by the air bubble in 3 minutes. The plus and minus signs in the *b* columns indicate the charge of the set gel.

TABLE I.

p_H.	*b*.	p_H.	*b*.	p_H.	*b*.
3·6	0·8(+)	6·0	0·6(−)	8·0	1·6 (−)
4·2	0·3(+)	6·6	0·9(−)	8·8	1·85(−)
4·8	0·0	7·0	1·2(−)		
5·2	0·2(−)	7·4	1·4(−)		

The above results show that gelatin has only one isoelectric point, in the neighbourhood of p_H 4·8. Below that it is positively charged and the charge increases as the p_H diminishes. Above p_H 4·8 the negative charge on the diaphragm increases with the rise in p_H within the range investigated. There is thus no indication of neutralisation of the negative charge of the substance at p_H 7·7. In view of the recent observations of Kruyt and Tendeloo (*J. Physical Chem.*, 1925, **29**, 1303), it might be thought that the multivalent phosphate ion had some influence on the negative charge of gelatin. Experiments were therefore performed using sodium hydroxide solution alone. The results are given in Table II; they, too, show no indication of an inversion in the electrokinetic potential of gelatin at p_H 7·7.

TABLE II.

p_H	7·0	7·6	8·6
b	1·0(–)	1·3(–)	1·7(–)

The above experiments also throw light on the structure of gelatin gels. There are different views regarding their structure: (1) Procter, Wilson, Katz, and others believe that gels form a sort of homogeneous solid solution; (2) Wo. Ostwald and others consider them to be two-phase liquid–liquid systems; (3) many others think that gels are two-phase solid–liquid systems and have an open network-like structure. Hatschek (Faraday Soc. Discussion, October, 1921) has shown that the mechanical properties of gels cannot be explained on the basis of the two-phase liquid–liquid theory of structure. In our experiments the occurrence of electro-endosmotic flow of water through a gelatin gel when it is used as the diaphragm material has been definitely established. This fact seems inexplicable on the solid-solution theory. It points to the conclusion that gelatin gel must have a porous capillary-like structure. The gelatin forms the solid walls of the capillaries and the pores are filled with the electrolyte solution. When an electric field is applied across a diaphragm of the gel, the liquid flows through the zig-zag system of capillaries. The above experiments therefore furnish strong evidence in favour of the third view of gel structure.

My best thanks are due to Prof. J. N. Mukherjee for his advice and encouragement.

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[*Received, April 8th*, 1927.]

CLXXIII.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Systems. Part II. The Substituted Succinimides.*

By SARBBANI SAHAY GUHA SIRCAR.

IN Part I (this vol., p. 600) evidence was brought forward of the well-marked influence of substituents in modifying the stabilities of substituted glutarimides. The present work deals with the velocity of hydrolysis of the substituted succinimides, containing a five-membered ring. Table I, giving the velocity coefficients for these compounds calculated for a bimolecular reaction, clearly shows the close general agreement of the experimental results with the requirements of the modified strain theory. There are, however, several other points of interest in the investigation. For example, the methyl group is found to produce an abnormal increase in the stability of the ring. This abnormality, although present in the glutarimide series, was masked by the unusually high value of the velocity coefficient for glutarimide itself. The anomalous behaviour of methyl in comparison with other alkyl groups is well known, particularly its influence on the dissociation constants of various series of acids (compare *Rec. trav. chim.*, 1912, **31**, 86; J., 1925, **127**, 342). A second point of interest is that the velocity coefficient for the first member of the series of succinimides is very nearly the same as the coefficients for the last two members. It seems as if the limit of stability of this system is reached in succinimide, or as if the *cyclo*pentane and the *cyclo*hexane rings are behaving like strainless systems, contributing little towards increasing the strain in the imide ring.

TABLE I.

Substituents.	$k \times 10^6$.
H,H	232
Me,H	141
Et,H	512
Me,Me	308
Me,Et	288
Et,Et	247
*cyclo*Pentane	235
*cyclo*Hexane	226

TABLE II.

Substance.	$k \times 10^6$.
Phthalimide	8,700
Homophthalimide	12,600
trans-Hexahydrophthalimide	26,500
trans-Hexahydrohomophthalimide	4,980
trans-*cyclo*Pentane-1-carboxy-2-acetimide	6,460

The study of a number of associated ring systems in which the hetero-ring is attached to the carbocyclic ring by two carbon atoms is not without interest. The velocity coefficients are in Table II. The associated systems seem to be less stable than the corresponding *spiro*-systems. This is a logical consequence of the strain theory if it is assumed that during the formation of the ring from the open chain the approximation of the ends of the chain (brought about by the influence of the substituents) may go beyond the requirement of closest spatial proximity; in other words, that the ends of the chain may overlap. In such a case the molecular strain would tend to increase rather than diminish as the effect of the substituent on the individual carbon atom becomes greater. It is also evident that the order of stability in passing from the five- to the six-membered ring may be reversed by this overlapping, making hexahydrohomophthalimide more stable than the lower homologue. In phthalimide and its homologue, however, the internally compensated (either by conjugation or by the mobility of the bonds) benzene nucleus prevents any rigid or permanent alteration in the extracyclic bonds, and the order of stability is the same as in the unsubstituted succinimide and glutarimide.

EXPERIMENTAL.

Preparation of the Imides.—All the imides were prepared by the method described in Part I (*loc. cit.*). Their structures were confirmed by regenerating the parent acids by hydrolysis with alkali.

Succinimide, m. p. 126° (Found: N, 14·4. Calc.: N, 14·1%). Methylsuccinimide, m. p. 66° (Found: N, 12·1. Calc.: N, 12·4%). Ethylsuccinimide, m. p. 77° (Found: N, 11·3. Calc.: N, 11·0%). *as*-Dimethylsuccinimide crystallised from hot water in scales, m. p. 106° (Found: N, 11·1. Calc.: N, 11·0%).

as-*Methylethylsuccinimide* was redistilled and then crystallised from acetone–ether; m. p. 64—65° (Found: N, 9·5. $C_7H_{11}O_2N$ requires N, 9·9%).

as-*Diethylsuccinimide.*—The acid was prepared by a slight modification of Higson and Thorpe's method (J., 1906, **89**, 1456) suggested by Dr. S. B. Dutt (private communication). A mixture of ethyl α-cyano-ββ-diethylacrylate (36 g.) (Birch and Kon, J., 1923, **123**, 2440), alcohol (400 c.c.), and potassium cyanide (15 g. in 30 c.c. of water) was kept for 2 weeks. The alcohol was then distilled off and the solution acidified. The heavy oil thus obtained could not be distilled in a vacuum without decomposition; so it was hydrolysed by boiling it with concentrated hydrochloric acid (5 vols.) for 10 hours under reflux. The material extracted from the cooled solution by ether was itself extracted with sodium carbonate solution,, which was then filtered, acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. The oily residue obtained on evaporation of the dried extracts soon solidified; it was then crystallised from dilute hydrochloric acid and again from benzene–petrol, the yield of the acid, m. p. 108°, being 20%. The *imide* crystallised from hot water in needles, m. p. 85—86° (Found: N, 9·5. $C_8H_{13}O_2N$ requires N, 9·0%).

cyclo*Pentane*spiro*succinimide* crystallised from water in plates, m. p. 124° (Found: N, 8·8. $C_8H_{11}O_2N$ requires N, 9·1%).

cyclo*Hexane*spiro*succinimide.*—The imide crystallised from hot water has m. p. 145° (Found: N, 8·25. $C_9H_{13}O_2N$ requires N, 8·3%).

Phthalimide, m. p. 229°. The velocity coefficient obtained by Miolati, *viz.*, 0·087, was utilised.

trans-*Hexahydrophthalimide.*—Hexahydrophthalic acids (*cis*- and *trans*-), prepared by Baeyer's method (*Annalen*, 1890, **258**, 145; 1892, **269**, 145), gave the same imide on distillation of the dry ammonium salts. This is regarded as the trans-*imide*, as it gives the *trans*-

acid on hydrolysis. It crystallised from hot water in large, glistening scales, m. p. 163—164° (Found: N, 9·4. $C_8H_{11}O_2N$ requires N, 9·2%).

Homophthalimide.—The acid, m. p. 173—174°, was prepared by reducing phthalonic acid with hydriodic acid and red phosphorus (*Ber.*, 1898, **31**, 369). The *imide* crystallised from hot water in scales, m. p. 75° (Found: N, 8·2. $C_9H_7O_2N$ requires N, 8·7%).

trans-*Hexahydrohomophthalimide.*—The acid (1-carboxy*cyclo*hexane-2-acetic acid) was prepared by Dutt's method (unpublished work), by condensing ethyl sodiocyanoacetate with ethyl Δ^1-tetrahydrobenzoate, and hydrolysing the resulting cyano-ester (b. p. 216°/20 mm.) by boiling it with concentrated hydrochloric acid (5 vols.) for 18 hours. (If the heating is less prolonged, a difficultly separable mixture of *cis*- and *trans*-acids is obtained.) The *trans*-acid thus formed (also described by Windaus, *Ber.*, 1923, **56**, 90) melted at 158° (Found: C, 58·1; H, 7·3. Calc.: C, 58·0; H, 7·6%). The *imide* crystallised from hot water in scales, m. p. 185° (Found: N, 8·0. $C_9H_{13}O_2N$ requires N, 8·4%).

trans-cyclo*Pentane*-1-*carboxy*-2-*acetimide* was prepared by a method similar to the previous one. *Ethyl* Δ^1-cyclo*pentenecarboxylate* was prepared by treating ethyl *cyclo*pentan-1-ol-1-carboxylate with phosphorus pentachloride and heating the product with diethylaniline (1·2 mols.) for 3 hours at 200°; it boiled at 92°/25 mm. and the yield was about 50% (Found: C, 68·3; H, 8·5. $C_8H_{12}O_2$ requires C, 68·5; H, 8·5%). The unsaturated ester (1 mol.) was treated with ethyl cyanoacetate (1 mol.) in presence of sodium ethoxide (1 mol.) dissolved in alcohol, and the mixture was heated on the steam-bath for 6 hours. The addition *compound* (yield 35%), which boiled at 185—186°/17 mm. (Found: C, 61·3; H, 7·4. $C_{13}H_{19}O_4N$ requires C, 61·6; H, 7·5%), was boiled with concentrated hydrochloric acid for 18 hours. The organic *acid* was extracted with ether and recrystallised thrice from dilute hydrochloric acid and then from benzene–petrol (b. p. 60—80°). It melted at 158°, was presumably the *trans*-acid, and behaved similarly to the *cyclo*hexane analogue (Found: C, 55·4; H, 7·1. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). The *imide* crystallised from petrol–ether in scales, m. p. 184—185° (Found: N, 9·4. $C_8H_{11}O_2N$ requires N, 9·15%).

Hydrolysis of the Imides.—*N*/190-Solutions of the imides were hydrolysed in the manner described in Part I (*loc. cit.*, p. 602). The results are in Table III, the letters having the same significance as before. Where $a = 10$, *N*/200-acid was used in the titrations; where $a = 5$, *N*/100-acid was used. For small velocity coefficients, titrations were made at intervals of 10 minutes.

TABLE III.

Succinimide
($a = 10$).

t.	$a-x$.	$k \times 10^6$.
0	10·0	—
5	9·9	(202)
10	9·75	256
20	9·55	232
30	9·35	234
40	9·15	232
50	9·0	202
60	8·75	235
70	8·6	232

Mean 232
(Miolati's value, 238)

Methylsuccinimide
($a = 10$).

t.	$a-x$.	$k \times 10^6$.
0	10·0	—
10	9·85	152
20	9·75	128
30	9·6	139
40	9·5	132
50	9·4	127
60	9·15	153
70	9·0	157
80	8·8	(174)
100	8·5	(176)

Mean 141
(Miolati's value, 135)

Ethylsuccinimide
($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	4·85	—
5	4·8	(833)
10	4·75	526
15	4·6	550
20	4·55	494
25	4·45	494
30	4·35	498

Mean 512

as-Dimethylsuccinimide
($a = 5$).

0	5·2 ?	—
5	5·0 ?	—
10	4·9	(204)
15	4·8	277
20	4·7	319
25	4·65	301
35	4·5	317
40	4·425	322

Mean 308

as-Methylethylsuccinimide ($a = 10$).

0	10·0	—
10	9·7	309
20	9·45	264
30	9·25	270
40	8·95	307
50	8·75	285
60	8·5	293

Mean 288

as-Diethylsuccinimide
($a = 10$).

0	10·0	—
5	9·8	(409)
10	9·75	256
20	9·5	263
30	9·35	231
40	9·1	247
50	8·9	247
60	8·7	241

Mean 247

*cyclo*Pentane*spiro*-succinimide ($a = 5$).

0	—	—
5	4·95	(202)
10	4·85	(307)
15	4·80	263
20	4·775	233
25	4·725	232
35	4·6	248

Mean 235

*cyclo*Hexane*spiro*-succinimide ($a = 5$).

0	5·0	—
5	4·95	(202)
10	4·85	(307)
15	4·80	263
20	4·75	232
25	4·725	217
35	4·65	215
46	4·55	—

Mean 226

trans-Hexahydrophthalimide ($a = 5$).

0	4·5	Excess.
5	2·1	26,600
10	1·35	27,000
15	1·0	26,600
20	0·75	28,300
25	0·65	26,000
30	0·60	24,400

Mean 26,500

Homophthalimide
($a = 5$).

0	3·7	—
5	2·8	(15,700)
10	2·25	12,700
15	1·75	12,300
20	1·4	12,800
25	1·15	12,700
30	1·05	12,500
35	0·90	13,000

Mean 12,600

trans-Hexahydrohomophthalimide
($a = 5$).

0	4·75	—
5	4·05	4690
10	3·5	4300
15	3·05	4260
20	2·4	5410
25	2·15	5300
32	1·8	5500
39	1·4	5400

Mean 4980

trans-*cyclo*-Pentane-1-carboxy-2-acetimide
($a = 5$).

0	4·3	—
5	3·8	6310
10	3·1	6130
15	2·5	6160
20	2·15	6130
25	1·8	7100
30	1·6	7080
35	1·4	6320

Mean 6460

The author wishes to express his grateful thanks to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in this work, and to the Chemical Society for a grant that partly defrayed the cost.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
[*Received, March 9th,* 1927.]

CLXXIV.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Systems. Part III. The Substituted Paraconic Acids.*

By SARBBANI SAHAY GUHA SIRCAR.

THE stability of five- and six-membered heterocyclic systems containing nitrogen having been examined (this vol., pp. 600 1252), a study has been made of five-membered rings containing oxygen. For this purpose the substituted paraconic acids were suitable. Three disubstituted acids had already been prepared by Birch, Gough, and Kon (J., 1921, **119**, 1320), and two others (methylethyl and *cyclo*pentane compounds) were obtained from the corresponding ketones by their method. The monosubstituted paraconic acids were prepared by Fittig's well-known method.

As paraconic acid and its monoalkyl derivatives can be neutralised at the ordinary temperature without fission of the lactone ring, which is only attacked by hot alkali (Fittig, *Ber.*, 1890, **23**, 91), it was possible in the present investigation to use two equivalents of alkali, one to neutralise the acid and the other to effect the opening of the ring; the first process, being instantaneous, had no undesirable effect on the hydrolysis. At 25° the velocity of hydrolysis was conveniently rapid in the solution prepared by adding 10 c.c. of $N/10$-sodium hydroxide to 90 c.c. of an $N/180$-solution of a paraconic acid.

The results of the hydrolyses given in Table I again show strikingly the influence of substituents on the stability of a heterocyclic system. The introduction of a methyl group causes, as was also observed in the two previous investigations, an increase in the stability. The influence of two ethyl groups is, however, greater than that of the *cyclo*pentane or *cyclo*hexane group.

TABLE I.

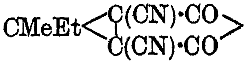
Substituents.	$k \times 10^5$.	Substituents.	$k \times 10^5$.
H, H	1630	Me, Et	164
Me, H	763	Et, Et	74·5
Et, H	652	*cyclo*Pentane	119
Me, Me	270	*cyclo*Hexane	107

EXPERIMENTAL.

Paraconic acid was prepared by decomposing itabromopyrotartaric acid by water (*Annalen*, 1882, **216**, 77; in the preparation of itabromopyrotartaric acid by the addition of hydrobromic acid to itaconic acid it was found convenient to heat the mixture at

100° for 3 hours) and purified by means of the silver salt. The acid was very hygroscopic; m. p. 57° (Found: C, 45·8; H, 5·0. Calc.: C, 46·15; H, 4·6%). Methylparaconic acid (Fittig, *Ber.*, 1890, **23**, 91) was slightly hygroscopic; m. p. 84·5° (Found: C, 49·8; H, 5·8. Calc.: C, 50·0; H, 5·55%). Ethylparaconic acid (Fittig, *loc. cit.*) had m. p. 85° (Found: C, 53·0; H, 6·6. Calc.: C, 53·2; H, 6·3%). Dimethylparaconic acid (terebic acid) (Birch, Gough, and Kon, *loc. cit.*) crystallised from water in scales, m. p. 174° (Found: C, 53·4; H, 6·4. Calc.: C, 53·1; H, 6·4%). Diethylparaconic acid (Birch and Thorpe, J., 1922, **121**, 1825) had m. p. 105° (Found: C, 57·85; H, 7·4. Calc.: C, 58·05; H, 7·5%). *cyclo*Hexane*spiro*paraconic acid (Birch, Gough, and Kon, *loc. cit.*) had m. p. 184—185° (Found: C, 60·3; H, 7·4. Calc.: C, 60·6; H, 7·1%).

Methylethylparaconic Acid.—This acid was prepared by a method similar to that employed in preparing the dimethyl compound (above). Details are not given, as they differed only in minor points from those recorded by Birch, Gough, and Kon. The *imide*,



$CMeEt\left<\begin{matrix}C(CN)\cdot CO\\ C(CN)\cdot CO\end{matrix}\right>NH$, was crystallised from alcohol; m. p. 225—227° (Found: N, 20·4. $C_{10}H_9O_2N_3$ requires N, 20·7%). 2 : 3-*Dicyano*-1-*methyl*-1-*ethyl*cyclo*propane*-2-*carboxyiamide* crystallised from benzene in needles, m. p. 127—128° (Found: N, 23·4. $C_9H_{11}ON_3$ requires N, 23·7%). The γ-*lactone* of β-*hydroxy*-β-*ethylbutane*-γδδ-*tricarboxylic acid* crystallised from water on the addition of hydrochloric acid, m. p. 157—158° (efferv.) (Found: C, 49·7; H, 5·6. $C_9H_{12}O_6$ requires C, 50·0; H, 5·55%). *Methylethylparaconic acid* crystallised from hot water in needles, m. p. 131—132° (Found: C, 55·45; H, 6·7. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%. Found for the *silver* salt: Ag, 38·4. $C_8H_{11}O_4Ag$ requires Ag, 38·7%).

cyclo*Pentane*spiro*paraconic Acid.*—The preparation was similar to that of the *cyclo*hexane analogue (above). The bridged *imide* was crystallised from alcohol; m. p. 202—203° (Found: N, 20·3. $C_{11}H_9O_2N_3$ requires N, 20·9%). cyclo*Pentane*spiro-2 : 3-*dicyano*-cyclo*propane*-2-*carboxylamide* was crystallised from dilute alcohol; m. p. 126° (Found: N, 21·8. $C_{10}H_{11}ON_3$ requires N, 22·2%). The γ-*lactone* of 1-*hydroxy*cyclo*pentylethane*-αββ-*tricarboxylic acid* slowly crystallised from a small quantity of water after the addition of hydrochloric acid; m. p. 175—177° (efferv.). cyclo*Pentane*-spiro*paraconic acid* was prepared by heating the tribasic acid at 200° for 2 hours until the evolution of carbon dioxide ceased; it crystallised from water in needles, m. p. 127° (Found: C, 58·3; H, 6·4. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%. Found for the *silver* salt: Ag, 37·4. $C_9H_{11}O_4Ag$ requires Ag, 37·1%).

Details of the hydrolyses are recorded in Table II. $a = 5$ in all cases. (For the meaning of the letters, see preceding paper.)

TABLE II.

	Paraconic acid.		Methylparaconic acid.		Ethylparaconic acid.		Dimethylparaconic acid.	
t.	$a-x$.	$k\times 10^5$.	$a-x$.	$k\times 10^5$.	$a-x$.	$k\times 10^5$.	$a-x$.	$k\times 10^5$.
0	3·1	—	4·7	—	4·2	—	5·0	—
5	2·8	1430	3·7*	(878)	3·3	(857)	4·4	272
10	1·75	1850	2·8	788	2·75	743	3·9	266
15	1·35	1800	2·3	780	2·35	704	3·55	272
20	1·15	1670	2·0	750	2·2	606	3·2	271
25	1·0	1600	1·8	761	1·9	629	3·0	266
30	0·9	1510	1·55	772	1·65†	601	2·8	252
35	0·8	1560	1·35	730	1·5‡	630	2·5	285
	Mean	1630	Mean	763	Mean	652	Mean	270

t.	Methylethylparaconic acid.		Diethylparaconic acid.		*cyclo*Pentane-*spiro*paraconic acid.		*cyclo*Hexane-*spiro*paraconic acid.	
0	4·8	—	5·0	—	4·95	—	5·2	—
5	4·6	174	4·9	(41)	4·6	(174)	4·95	(202)
10	4·3	162	4·7	64	4·45	124	4·5	111
15	4·05	155	4·5	74	4·2	127	4·35	100
20	3·8	163	4·35	75	4·0	125	4·1	102
25	3·55	171	4·2	76	3·9	113	3·9	112
30	3·3	163	4·05	78	3·7	117	3·75	111
35	3·15	168	3·95	76	3·6	111	3·6	155
40	—	—	3·8	79	—	—	—	—
	Mean	164	Mean	74·5	Mean	119	Mean	107

*, †, ‡ values for 4, 31, and 37 minutes, respectively.

The author wishes to express his grateful thanks to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in the work and to the Chemical Society for a grant that partly defrayed the cost.

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LONDON, S.W. 7.
[*Received, March 9th*, 1927.]

CLXXV.—*Researches on Residual Affinity and Co-ordination. Part XXIX. Cupric Salts Stabilised by Ethylenediamine.*

By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

ALTHOUGH cupric salts of the more strongly electronegative anions are stable exothermic compounds, this condition of stability depends largely on the nature of the acidic ions, and as their electronegative character diminishes, the normal cupric salts exhibit an increasing tendency to decompose either by hydrolytic change or by a spontaneous decrease of valency from bivalent to univalent copper.

The former mode of decomposition is exhibited by cupric carbonate, the latter by cupric iodide ($CuI_2 = CuI + I + 11{,}560$ cals.).

In earlier experiments on this subject (J., 1926, 2018, 2027) it was shown that cupric iodide can be stabilised by combination with ethylenediamine, and accordingly we have employed this new reagent $[Cu,2\,en,2H_2O]I_2$ in a further study of cupric salts of the weaker acids.

Amminated Cupric Carbonates.—The normal salt, $CuCO_3$, has not hitherto been obtained, since both laboratory methods and geological processes lead to the formation of basic carbonates. A double carbonate of normal type, $K_2[Cu(CO_3)_2]$, was obtained in anhydrous and hydrated forms by Reynolds (J., 1898, **73**, 262), but this substance is readily decomposed by water. A compound having the composition $CuO,3CO_2,4NH_3$ is described by Maumené (*Compt. rend.*, 1882, **95**, 225), and the diamminocupric carbonate, $CuCO_3,2NH_3$, by Favre (*Ann. Chim. Phys.*, 1844, **10**, 116). With the reagents cooled to – 18°, Ephraim isolated pentamminocupric carbonate, $CuCO_3,5NH_3$, which at 37° dissociated into the diammine (*Ber.*, 1919, **52**, 940).

By interaction between silver carbonate and aqueous bisethylenediamminocupric iodide we have now obtained *bisaquobisethylenediamminocupric carbonate*, $[Cu,2\,en]CO_3,2H_2O$, as a well-defined salt, readily soluble in water or alcohol to solutions which can be boiled without decomposition of the product.

Amminated Cupric Nitrites.—Cupric nitrite has not been obtained in a stable form, for when it is prepared in aqueous media, complex changes occur and nitric oxide is evolved at the ordinary temperature. A basic salt, $Cu(NO_2)_2,3Cu(OH)_2$, has been isolated (van der Meulen, *Ber.*, 1879, **12**, 758) and double nitrites such as $K_3[Cu(NO_2)_5]$ and $Tl_3[Cu(NO_2)_5]$ have been described (Kurtenacker, *Z. anorg. Chem.*, 1913, **82**, 204; Cuttica and Paciello, *Gazzetta*, 1922, **52**, i, 141). An amminated compound formerly described by Péligot (*Compt. rend.*, 1861, **53**, 209) as hydrated diamminocupric nitrite has since been proved by Bassett and Durrant to be anhydrous tetramminocupric nitrite,* $[Cu,4NH_3](NO_2)_2$, which at 97° dissociates into the anhydrous diammine $Cu(NH_3)_2(NO_2)_2$ (J., 1922, **121**, 2636).

Interaction between silver nitrite and diaquobisethylenediamminocupric iodide leads to *bisethylenediamminocupric nitrite*, an anhydrous, well-defined salt stable up to 120° and in boiling aqueous or alcoholic solutions.

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* In Hoffmann's "Lexikon" and Gmelin-Kraut's "Handbuch der anorganischen Chemie," [VII], V, i, pp. 1569, 1123, 1576, 1578, references are given to the preparation by Pudschies of tetramminocupric nitrite, sulphite, and thiosulphate, but we have not been able to obtain the original publication (*Dissert.*, Strassburg, 1904).

Evidence was also gained of the existence of a similar complex cupric hyponitrite, although the compound was not isolated in a state of purity. A more decisive result was, however, obtained with cupric hypophosphite.

Bisethylenediamminocupric hypophosphite, $[Cu,2\,en](H_2PO_2)_2$, is stable up to 115° and in aqueous or alcoholic solution. The reducing action of the hypophosphite ion on bivalent copper is far less noticeable than with cupric hypophosphite, which furnishes copper hydride.

Amminated Cupric Sulphites.—The normal salt, $CuSO_3$, has not been isolated with certainty, and the causes of its instability are similar to those inducing the decomposition of cupric nitrite. Reduction of the cupric ion by the sulphite radical leads to the formation of cuprous compounds and the precipitation of sparingly soluble, red cupric cuprososulphite, $Cu(CuSO_3)_2,2H_2O$.

The stability of cupric sulphite is enhanced by ammination, for the tetrammine, $[Cu,4NH_3]SO_3,2H_2O$, is recorded by Pudschies (*loc. cit.*).

We have now obtained two ethylenediamine derivatives of normal cupric sulphite: *Monoaquoethylenediamminocupric sulphite*, $[Cu,en,H_2O]SO_3$, by the action of aqueous ethylenediamine on cupric cuprososulphite, and *bisethylenediamminocupric sulphite*, $[Cu,2\,en]SO_3$, by adding copper to a suspension of silver sulphite in ethylenediamine. The latter method is of general application in the preparation of amminated cupric salts.

The chemical properties of the foregoing complex cupric sulphites indicate clearly that the more fully co-ordinated compound, $[Cu,2\,en]SO_3$, is much the more stable of the two.

Amminated Cupric Thiosulphates.—A reducing action of the cupric ion occurs in interactions between soluble cupric salts and alkali thiosulphates, so that normal cupric thiosulphate has not hitherto been isolated. Amminated derivatives have, however, been recorded. Pudschies (*loc. cit.*) cites the tetrammine, $[Cu,4NH_3]S_2O_3$, and a more complex binuclear salt, $[Cu_2,3\,en,2H_2O](S_2O_3)_2$, is described by Benrath (*Z. anorg. Chem.*, 1917, **99**, 5).

Bisethylenediamminocupric thiosulphate, $[Cu,2\,en]S_2O_3$, which is stable up to 130°, is prepared by double decomposition between barium thiosulphate and bisethylenediamminocupric sulphate.

Amminated Cupric Polythionates.—Cupric dithionate crystallising with 4 or 5 molecules of water has long been known (Heeren, *Pogg. Annalen*, 1826, **7**, 181; Grailich and Murmann, *Ber. Wien. Akad.*, 1857, **27**, 171); it decomposes readily to a basic salt,

$[Cu,3Cu(OH)_2]S_2O_6$, of the atacamite type (compare the basic nitrite, p. 1260).

Two amminated derivatives of cupric dithionate are described: the tetrammine, $[Cu,4NH_3]S_2O_6$ (Heeren, *loc. cit.*; Schweitzer, *J. pr. Chem.*, 1856, **67**, 430; Horn, *Amer. Chem. J.*, 1908, **39**, 212), and the monoammine, obtained by the last-mentioned investigator from the tetrammine and liquid ammonia.

Bisethylenediamminocupric dithionate, $[Cu,2\,en]S_2O_6$, is a well-defined, sparingly soluble salt remaining undecomposed up to 280°. When trithionates and cupric salts interact in warm aqueous solution, copper sulphide is precipitated. Ammonia derivatives of cupric trithionate are not recorded, but stabilisation of this salt has now been obtained by the isolation of *bisethylenediamminocupric trithionate*, $[Cu,2\,en]S_3O_6$, stable up to 170°.

Cupric tetrathionate has been prepared by adding copper carbonate to Wackenroder's solution (Curtis and Hinkel, *J. pr. Chem.*, 1888, **37**, 148), but the only amminated derivative on record is the tetrapyridine compound $[Cu,4Py]S_4O_6$ (Calzolari, *Atti R. Accad. Lincei*, 1915, **24**, i, 921).

Bisethylenediamminocupric tetrathionate, $[Cu,2\,en]S_4O_6$, is a well-defined salt stable up to 160°.

The foregoing complex cupric polythionates which have the same general formula $[Cu,2\,en]S_xO_6$ exhibit a well-marked gradation of physical and chemical properties. As the sulphur accumulates in the molecule, the colour of the salt deepens, its solubility in water increases, and its decomposition temperature decreases.

Owing to the destructive action of ethylenediamine on alkali pentathionates from Wackenroder's solution, the complex cupric pentathionate of this series was not isolated. Other attempts made to complete the series of ethylenediamminocupric salts of sulphur oxy-acids were unsuccessful as regards hydrosulphurous acid, $H_2S_2O_4$, and formaldehydesulphoxylic acid, $CH(OH)HSO_2$, but the corresponding salt of persulphuric acid was isolated.

Amminated Cupric Persulphates.—Cupric persulphate has not been isolated, but its tetrammino- and tetrapyridine-derivatives, $[Cu,4\,base]S_2O_8$, have been prepared (Barbieri and Calzolari, *Z. anorg. Chem.*, 1911, **71**, 347).

Bisethylenediamminocupric persulphate, $[Cu,2\,en]S_2O_8$, is a sparingly soluble salt comparable in its explosive properties with ethylenediamminocupric perchlorate (J., 1926, 2026).

Bisethylenediamminocupric selenocyanate, $[Cu,2\,en](CNSe)_2$, furnishes a noteworthy example of the stabilising effect of ethylenediamine on a very decomposable cupric salt. Interaction of soluble selenocyanates and cupric salts leads to the precipitation of copper selenide, both cupric and cuprous selenocyanates being unstable under these conditions. When, however, ethylenediamine is present, the separation of copper selenide is inhibited, and the complex salt, $Cu(CNSe)_2,2\,en$, is obtained in stable, well-defined, anhydrous crystals.

Co-ordination Numbers of Bivalent Copper.

Of the eleven complex cupric salts described in this communication, ten contain two molecular proportions of ethylenediamine to one atomic proportion of copper, and of these ten salts, nine are anhydrous and include no other addenda than the diamine. Of the two anomalous salts, the sulphite $[Cu, en, H_2O]SO_3$ may be regarded as co-ordinatively unsaturated, whereas the dihydrated carbonate, $CuCO_3,2\,en,2H_2O$, is of ambiguous character, with a co-ordination number for copper ranging from 4 to 6, according to the allocation of the two molecules of water between kation and anion.

In the other nine cases of anhydrous salts having the general formulæ $[Cu,2\,en]X_2'$ and $[Cu,2\,en]X''$ (X' and X'' being monobasic and dibasic anions), the experimental evidence points to a co-ordination value of 4 for bivalent copper as being the predominant type most conducive to molecular stability.

From the wide range of derivatives examined, it is obvious that the stability of this fourfold co-ordination is not appreciably influenced either by the chemical nature or by the valency of the anion. The recurrence of the co-ordination complex with two implicated ethylenediamine molecules suggests the influence of forces making for symmetrical orientation of the two chelate groups. The discovery by Mills and Gotts of optical activity among copper compounds having a co-ordination number of 4 (J., 1926, 3124) affords direct proof of tetrahedral arrangement of the four associating units round the central copper atom. It is accordingly highly probable that in the bisethylenediamminocupric salts described below, a tetrahedral arrangement of the two chelate diamine groups is also present.

Regarded from the electronic point of view, the co-ordination complex $[Cu,2\,en]''$ is still unsaturated, since the bivalent cupric ion with electronic structure 2,224,22445 (Main Smith, *J. Soc. Chem. Ind.*, 1924, **43**, 323) shares eight additional electrons with the two ethylenediamines, thereby giving to the co-ordinated atom the electronic structure 2,224,22445,224, which differs from the arrangement 2,224,22446,224 for krypton, the next inert gas, in a shortage of one electron in the ninth sub-group. Any addendum supplying one additional electron would complete the inert-gas structure with a co-ordination number of 5.

As, however, many 6-co-ordinated cupric complexes are also known, it is evident either that an electronic structure with three electrons in excess of krypton is possible, or, alternatively, that certain of the six associating units are contributing only one electron each, instead of the two which are generally regarded as operative in a non-polar linking.

It seems evident from a general survey of co-ordinated copper compounds that the forces making for symmetrical arrangement (co-ordination numbers 4 and 6) prevail over forces tending to reproduce the electronic structure of an inert gas. The co-ordination number 4 offers, in the case of the cupric ion, the optimum condition as regards symmetrical arrangement of associating units, coupled with a very close approximation to the saturated electronic structure of krypton.

EXPERIMENTAL.

Bisaquobisethylenediamminocupric Carbonate, [Cu,2 en]CO_3,$2H_2O$.—A concentrated aqueous solution of hydrated bisethylenediamminocupric iodide, [Cu,2 en,$2H_2O$]I_2, was triturated with a slight excess of freshly prepared silver carbonate. The purple filtrate was treated with alcohol–ether; the complex carbonate was then precipitated. Recrystallised from water after the addition of alcohol and ether, this salt separated as a very hygroscopic, purple, crystalline powder, m. p. 135° (decomp.), readily soluble in water or alcohol (Found in material dried over sulphuric acid: C, 21·2; H, 7·3; N, 19·8; Cu, 23·1. $C_5H_{20}O_5N_4Cu$ requires C, 21·45; H, 7·2; N, 20·0; Cu, 22·7%).

Aqueous or alcoholic solutions of this complex normal carbonate could be boiled without decomposition and were stable in the presence of caustic alkali, but were decomposed by dilute acids. Silver nitrate produced in them an immediate precipitation of silver carbonate even in the cold, thus indicating the ionised condition of the dissolved complex salt.

Bisethylenediamminocupric nitrite, [Cu,2 en]$(NO_2)_2$, was prepared by triturating together bisaquobisethylenediamminocupric iodide and freshly prepared silver nitrite (in slight excess); the filtrate from silver iodide was concentrated to a small bulk and left over sulphuric acid. The complex *nitrite* crystallised slowly from the syrupy solution in dark purple needles, which were purified by recrystallisation from water or alcohol, and also by reprecipitation from aqueous solution with ether and alcohol. After drying over sulphuric acid in a vacuum desiccator, the complex salt was anhydrous (Found: C, 17·9; H, 5·95; N, 29·9; Cu, 23·2; NO_2, 33·3. $C_4H_{16}O_4N_6Cu$ requires C, 17·4; H, 5·85; N, 30·5; Cu, 23·05; NO_2, 33·4%).

This complex nitrite, which melted with rapid decomposition at 128°, was extremely soluble in water, but less soluble in alcohol. In aqueous or alcoholic solution the salt was not decomposed even on boiling; caustic alkalis had no effect, but dilute acid caused immediate evolution of nitrous fumes. Silver nitrate produced a quantitative separation of silver nitrite in alcoholic solution, showing that the dissolved complex nitrite was ionised in this medium.

Attempted Preparation of an Ethylenediamminocupric Hyponitrite. —The replacement method (see p. 1266) employed in the case of the complex sulphite [Cu,2 en][SO_3] was tried with silver hyponitrite and metallic copper in the presence of ethylenediamine. Silver was deposited, and the resulting dark purple solution of complex cupric salts was concentrated to the crystallising point; purplish-blue plates were then obtained which had the composition of a complex cupric hyponitrite, [Cu,3 en][N_2O_2], mixed with the carbonate [Cu,2 en][CO_3,$2H_2O$], the latter being produced by absorption of carbon dioxide from the atmosphere. The impure salt dissolved readily in water, and on addition of silver nitrate the solution gave yellow silver hyponitrite.

Bisethylenediamminocupric Hypophosphite, [Cu,2 en](H_2PO_2)$_2$.—An aqueous solution of barium hypophosphite (5·3 g.) was added to one of copper sulphate (5·0 g.) containing ethylenediamine (2·4 g.), and the mixture shaken for some hours. After filtration from barium sulphate, the purplish-blue liquid was concentrated on the water-bath and left over concentrated sulphuric acid. The surface of the liquid soon became covered with a pale mauve, crystalline crust of hypophosphite, which was recrystallised from water and dried over sulphuric acid (Found: C, 15·7; H, 6·9; N, 17·9; P, 19·5; Cu, 20·5. $C_4H_{20}O_4N_4P_2Cu$ requires C, 15·3; H, 6·4; N, 17·85; P, 19·8; Cu, 20·3%).

Although this complex hypophosphite was hygroscopic, it remained unchanged when kept quite dry. On heating, the dry salt decomposed rapidly at 115—118° to a dark brown solid. It dissolved readily in alcohol; this solution was slowly decomposed in presence of sodium hydroxide, although the aqueous solution was unaffected. Hydrochloric and sulphuric acids caused decolorisation of the solution, and the latter acid gave a reddish precipitate of metallic copper. Silver nitrate solution gave a white precipitate in the cold, which darkened rapidly, with the separation of black metallic silver; in acid solution a silver mirror was obtained.

Bisethylenediamminocupric persulphate, [Cu,2 en]S_2O_8, was deposited in purplish-red, acicular crystals when aqueous potassium persulphate was added to an aqueous solution of copper sulphate

(1 mol.) containing ethylenediamine (2 mols.). The crystals were washed successively with cold water, alcohol, and dry ether and analysed immediately (Found: Cu, 16·8; S_2O_8, 51·0. $C_4H_{16}O_8N_4S_2Cu$ requires Cu, 16·9; S_2O_8, 51·15%).

The complex persulphate was extremely unstable, and when left in air or in the desiccator it decomposed, leaving a blue residue; one preparation exploded when contained in a cooled specimen tube. The salt detonated on percussion and exploded on heating or on warming with concentrated sulphuric acid.

Although only very sparingly soluble in cold water, the persulphate dissolved more readily on warming; the purple solution, which changed to blue without appreciable evolution of gas, yielded with barium salts a copious precipitate of barium sulphate. Silver nitrate gave no reaction in the cold, but, on warming, oxygen was evolved and the purple solution changed to blue. Concentrated hydrochloric acid caused decomposition with evolution of chlorine.

Monoaquoethylenediamminocupric Sulphite, [Cu, en,H_2O]SO_3.—The dark red cupric cuprososulphite prepared by warming a 20% solution of cupric sulphate with concentrated aqueous potassium bisulphite was shaken with a cold aqueous solution of ethylenediamine; a deep purple liquid was then obtained with deposition of copper. On addition of a considerable volume of alcohol to the filtered solution, the complex cupric sulphite separated in pale reddish-mauve nodules. The product was purified by solution in water and reprecipitation with alcohol. After drying over sulphuric acid, the salt was monohydrated (Found: C, 11·1; H, 5·0; N, 13·3; SO_3, 35·6; Cu, 28·5. $C_2H_{10}O_4N_2SCu$ requires C, 10·9; H, 4·5; N, 12·6; SO_3, 36·1; Cu, 28·7%).

The aqueous solution of the complex sulphite decomposed on warming to give a brown precipitate containing cuprous oxide; dilute sulphuric acid caused a separation of red metallic copper, whereas hydrochloric acid gave cuprous chloride, both reactions being accompanied by evolution of sulphur dioxide. On exposure to air this sulphite oxidised slowly; at 100° it blackened, and at higher temperatures its colour changed to brown.

Bisethylenediamminocupric Sulphite, [Cu,2 en]SO_3.—Metallic copper (2·5 g.) was added with constant stirring to a mixture of freshly prepared silver sulphite (11·8 g.), ethylenediamine (4·8 g.), and 50 c.c. of cold water. After being shaken for an hour, the mixture was filtered from metallic silver and the deep purple filtrate was evaporated to the crystallising point over sulphuric acid. Prismatic crystals of the complex sulphite slowly separated and the surface of the liquid became covered with a pale mauve crust of the salt. Recrystallisation from cold water and desiccation over sulphuric acid gave well-defined, mauve, opaque, tabular and pyramidal crystals with matt surfaces. This anhydrous sulphite decomposed without melting at 190—200° (Found: C, 18·4; H, 6·2; N, 20·9; S, 12·2; Cu, 24·2. $C_4H_{16}O_3N_4SCu$ requires C, 18·2; H, 6·1; N, 21·25; S, 12·15; Cu, 24·1%).

Although hygroscopic, the complex sulphite remained unchanged in a closed vessel; its aqueous solution was not visibly affected by boiling. In cold solutions of the salt, silver nitrate, and barium chloride produced, respectively, copious white precipitates of silver and barium sulphites. With sodium hydroxide the solution remained clear, but its colour changed from purple to blue; the colour was discharged by mineral acids.

Bisethylenediamminocupric Thiosulphate, $[Cu,2\,en]S_2O_3$.—An aqueous solution of cupric sulphate (5·0 g.) containing 2·4 g. of ethylenediamine was triturated with excess of barium thiosulphate (6·0 g.), and the mixture shaken for several hours. The purplish-blue filtrate was then concentrated and cooled; the blue plates of the complex cupric thiosulphate that separated were crystallised from water containing a few drops of ethylenediamine (Found: C, 16·0; H, 5·6; N, 18·75; S, 21·5; Cu, 21·2. $C_4H_{16}O_3N_4S_2Cu$ requires C, 16·2; H, 5·45; N, 18·9; S, 21·7; Cu, 21·5%).

The complex thiosulphate remained unchanged in air, but on heating it decomposed without melting at 150—155°. The stable purplish-blue solution in water became blue on addition of aqueous sodium hydroxide, whereas warm alcoholic soda precipitated cupric oxide. Silver nitrate gave a white precipitate, blackening rapidly even in the cold. Sulphuric and hydrochloric acids discharged the purplish-blue colour of the solution, in the former case with the formation of a brown precipitate.

Bisethylenediamminocupric Dithionate, $[Cu,2\,en]S_2O_6$. — When 4·8 g. of sodium dithionate, 5·0 g. of copper sulphate, and 2·4 g. of ethylenediamine were mixed together in aqueous solution, a purplish-red, crystalline precipitate separated which became anhydrous after drying over sulphuric acid (Found: C, 13·45; H, 4·9; N, 16·0; S, 18·2; Cu, 19·1. $C_4H_{16}O_6N_4S_2Cu$ requires C, 14·0; H, 4·7; N, 16·3; S, 18·65; Cu, 18·5%).

This complex cupric dithionate was quite stable in air at the ordinary temperature, and on heating it decomposed with blackening at 260°. It was only very sparingly soluble in cold water, but dissolved more readily on warming to a stable purple solution. Barium chloride and silver nitrate were without action on the hot or cold solution; with sodium hydroxide the colour was changed to blue, whereas with mineral acids it was discharged.

Bisethylenediamminocupric Trithionate, $[Cu,2\,en]S_3O_6$.—A cold aqueous solution of sodium trithionate (7·1 g.) was added to a cold solution of cupric acetate (5·9 g.) containing ethylenediamine (3·6 g.). The purple solution was filtered and an excess of alcohol added; the complex *trithionate* then separated in purple, matted needles. After recrystallisation from luke-warm water and desiccation over sulphuric acid, the trithionate was anhydrous (Found: C, 12·7; H, 4·5; N, 15·1; S, 25·9; Cu, 17·1. $C_4H_{16}O_6N_4S_3Cu$ requires C, 12·8; H, 4·3; N, 14·9; S, 25·6; Cu, 16·9%).

This salt was quite stable in the air under normal conditions, but on heating it decomposed without melting at 170—175°. Silver nitrate gave, in the cold, a white precipitate, rapidly becoming yellow and finally black; this decomposition was greatly facilitated by warming. Barium chloride had no action in the cold, but on heating a white precipitate was formed. Sodium hydroxide caused the purple aqueous solution to become blue, whereas dilute acids discharged the intense colour with deposition of copper sulphide.

Bisethylenediamminocupric Tetrathionate, $[Cu,2\,en]S_4O_6$.—An aqueous solution of 3·4 g. of cupric chloride, 2·4 g. of ethylenediamine, and 6·0 g. of sodium tetrathionate was cautiously concentrated and cooled; the large, deep purple, rhomboidal prisms that separated were crystallised from water. The original deposition of complex tetrathionate was preferably induced by the addition of alcohol to the original solution, thus obviating evaporation. When dried over calcium chloride, the salt was anhydrous (Found: C, 11·7; H, 4·1; N, 13·8; S, 31·5; Cu, 15·6. $C_4H_{16}O_6N_4S_4Cu$ requires C, 11·8; H, 3·95; N, 13·7; S, 31·4; Cu, 15·6%). The well-defined, prismatic crystals of this complex tetrathionate were permanent in air, but on heating at 160° they decomposed with blackening. The aqueous solution was stable even on boiling; silver nitrate gave a white precipitate which darkened rapidly; barium chloride had no effect, sodium hydroxide changed the colour from purple to blue, and mineral acids discharged it.

The foregoing complex salts of the oxy-acids of sulphur were all insoluble in alcohol and other organic media.

Attempts made to complete this series of polythionates by the preparation of an ethylenediamminocupric pentathionate were unsuccessful, owing to the destructive action of the diamine in removing sulphur from the alkali pentathionates obtained from Wackenroder's solution.

Bisethylenediamminocupric Selenocyanate, $[Cu,2\,en](CNSe)_2$.—To an aqueous solution of 5·19 g. of cupric chloride and 3·6 g. of ethylenediamine were added 8·6 g. of potassium selenocyanate, also dissolved in water. The purple solution was concentrated to a small bulk and cooled; bluish-purple, prismatic crystals of the complex *selenocyanate* then separated. By recrystallisation from water, large, compact crystals were obtained, which were dried over sulphuric acid (Found: C, 18·3; H, 4·2; N, 21·8; Se, 39·8; Cu, 16·6. $C_6H_{16}N_6Se_2Cu$ requires C, 18·3; H, 4·1; N, 21·3; Se, 40·2; Cu, 16·1%).

This complex cupric selenocyanate was stable in air at the ordinary temperature, but it darkened at 100° and melted at 159—160° to a deep blue liquid. The salt was moderately easily soluble in water to a purple solution, which could be boiled without change; it was only slightly soluble in alcohol. With either aqueous or alcoholic solutions, silver nitrate gave a copious white precipitate even in the cold. Mineral acids caused the deposition of elemental selenium. Aqueous or alcoholic soda did not effect any change in the cold, but on warming the alcoholic solution a precipitation of cupric oxide occurred.

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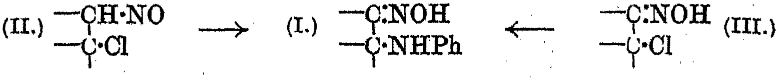
[*Received, March* 16*th*, 1927.]

CLXXVI.—*The Recovery of Pinene from its Nitrosochloride.*

By JOHN CAMPBELL EARL and JAMES KENNER.

THE observation by Wallach (*Annalen*, 1889, **252**, 132; 1890, **258**, **343**), that pinene can be regenerated from its nitrosochloride by heating this with aniline, has remained unique until the present time. All other nitrosochlorides which have been examined in this respect furnish nitrolanilides (I) :—

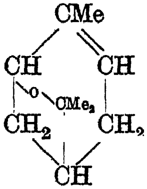


$$\text{(II.)}\ \begin{matrix}-\text{CH}\cdot\text{NO}\\ -\text{C}\cdot\text{Cl}\end{matrix} \longrightarrow \text{(I.)}\ \begin{matrix}-\text{C:NOH}\\ -\text{C}\cdot\text{NHPh}\end{matrix} \longleftarrow \begin{matrix}-\text{C:NOH}\\ -\text{C}\cdot\text{Cl}\end{matrix}\ \text{(III.)}$$

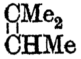
This applies equally to the bisnitrosochlorides such as those of limonene and pinol, which dissociate to a greater or less extent in solution into the unimolecular, blue nitroso-compounds (II), and also to the *iso*nitrosochlorides (III) exemplified by pinol *iso*nitrosochloride (Wallach and Sieverts, *Annalen*, 1899, **306**, 278). The nitrosochloride of trimethylethylene also exists in the two forms (Schmidt, *Ber.*, 1902, **35**, 3727), and again from each of these we have obtained by reactions conducted at the ordinary temperature a nitrolanilide agreeing in properties with that prepared by Schmidt from the nitrosonitrate (*Ber.*, 1902, **35**, 2339; also Wallach, *Annalen*, 1887, **241**, 296). These results, together with the close structural relationship of both pinol (IV) and trimethylethylene (V) to pinene

(VI), only serve to accentuate the exceptional nature of the reaction between aniline and pinene nitrosochloride.

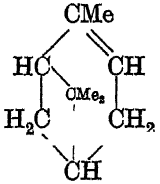
(IV.)



(V.)



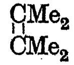
$$\mathrm{CMe_2{:}CHMe}$$



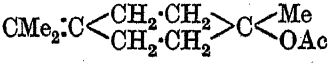
(VI.)

There is one class of nitrosochlorides the behaviour of which with aniline has not been investigated previously, namely, those which are constitutionally unable to pass into the *iso*nitroso-form. The derivatives of tetramethylethylene (VII) and γ-terpinyl acetate (VIII) were therefore examined in this respect, and both reproduced the behaviour of pinene.

(VII.)



$$\mathrm{CMe_2{:}CMe_2}$$



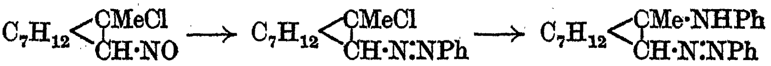
$$\mathrm{CMe_2{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CH_2}}{\mathrm{CH_2\cdot CH_2}}>\mathrm{C}<\genfrac{}{}{0pt}{}{\mathrm{Me}}{\mathrm{OAc}}$$

(VIII.)

The parent unsaturated compounds were recovered and identified by reconversion into the characteristic nitrosochlorides, and diazoaminobenzene was the other product of the reaction. But the velocity of reaction is much less in these cases than in that of pinene nitrosochloride, a difference which must be ascribed in part to the readiness with which the latter compound loses hydrogen chloride. For, as we have found, it is converted into nitrosopinene by simply boiling its solution in carbon tetrachloride, whereas Schmidt and Leipprand (*Ber.*, 1904, **37**, 545) observed that the nitrosobromide of tetramethylethylene is only slowly acted upon by aqueous potassium hydroxide. It is known that acids assist the condensation of aniline with nitrosobenzene, and, correspondingly, a comparative experiment showed that the interaction of aniline and tetramethylethylene nitrosochloride is accelerated by the addition of aniline hydrochloride at the outset. Even then, however, the velocity of reaction is much less than in the case of the pinene derivative, a point which will be referred to in more detail later.

Not only does hydrogen chloride accelerate, but it actually determines the course of the reaction in the case of pinene nitrosochloride. The formation of "nitrolamines" by the action of piperidine and the aliphatic amines (Wallach, *Annalen*, 1887, **241**, 296; 1888, **245**, 253; 1889, **252**, 107; 1891, **262**, 327) may be attributed to the greater efficiency of these bases, compared with aniline, in neutralising the hydrogen chloride which is necessarily liberated. For, as has now been found, *pinene nitrolanilide* is obtainable by allowing the interaction of the nitrosochloride and aniline to take place in the presence of either pyridine or sodium acetate. It is, however, essential that these reagents should be employed in a homogeneous solution. For when the reaction was allowed to proceed in chloroform solution in presence of either anhydrous sodium acetate or crystalline lead acetate, diazoaminobenzene was formed. This observation was, however, of value in that diazoaminobenzene had apparently not previously been isolated as such from this reaction, but only after conversion into aminoazobenzene.*

It would therefore seem that, whereas in nitrolanilide formation the chlorine is the first point of attack by the base, Wallach's reaction is due to the preferential reactivity of the nitroso-group, aided by a small proportion of hydrogen chloride derived from the chlorine atom :

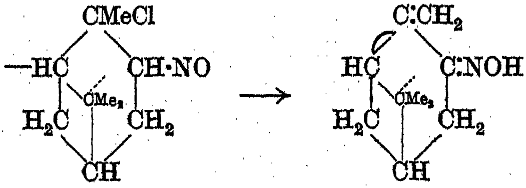


$$C_7H_{12}{<}\begin{matrix}CMeCl\\ CH\cdot NO\end{matrix} \longrightarrow C_7H_{12}{<}\begin{matrix}CMeCl\\ CH\cdot N{:}NPh\end{matrix} \longrightarrow C_7H_{12}{<}\begin{matrix}CMe\cdot NHPh\\ CH\cdot N{:}NPh\end{matrix}$$

(IX.) (X.)

The question whether the diazoaminobenzene originates in the reaction by the coupling of aniline with benzenediazonium chloride eliminated from the preliminary condensation product (IX), or from an anilide (X) derived from the latter, is for the present left in abeyance.

It remains to be explained why pinene nitrosochloride, in its usual behaviour towards aniline, ranges itself with the nitrosochlorides of tetramethylethylene and γ-terpinyl acetate rather than with those compounds to which its formula shows it to be more closely related, and which are capable of transition into the *iso*nitroso-form. It seems obvious that the reason for this peculiarity must be sought in the strained condition of the bonds uniting the central atom of the *gem*-dimethyl group with the rest of the pinene molecule. This produces a state of unsaturation which asserts itself in the conversion of pinene into sobrerol, and is very possibly responsible for the readiness, already mentioned, with which pinene nitrosochloride is converted into nitrosopinene :



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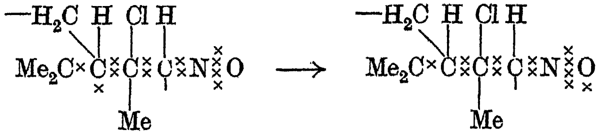
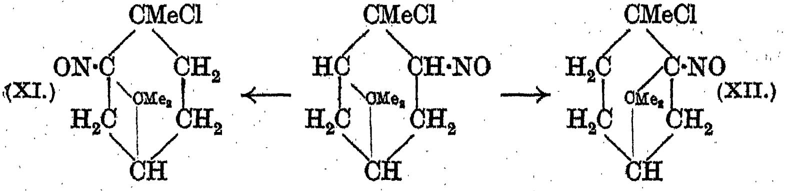
* In quite another direction also, this matter is one requiring further attention, since, in each of the experiments made, the diazoaminobenzene was first isolated in the labile form described by Walther (*J. pr. Chem.*, 1897, **55**, 551).

If, now, this unsaturation be transmitted as a general polar effect along the chain to the nitroso-group, the conditions are such as to enhance the unsaturation of the nitroso-group, as indicated by the following scheme (compare Robinson, *J. Soc. Chem. Ind.*, 1925, 456T):



It is therefore conceivable that the nitroso-group may be so reactive as to condense with aniline before passing into the *iso*nitroso-condition. At the same time, it must be emphasised that in the cases of pinol nitrosochloride and trimethylethylene nitrosochloride, already mentioned, where both forms are known, the nitroso- as well as the *iso*nitroso-isomerides are converted by aniline into nitrolanilides. Further, it is agreed that transmission of electronic displacement does not occur so readily through a saturated as through an unsaturated chain. For these reasons, it seems more plausible to assume that the condensation with aniline is preceded by a molecular rearrangement of the nitrosochloride such as to render it formally analogous to those compounds which it resembles in behaviour, and to confer the condition of unsaturation, already mentioned, on the carbon atom directly attached to the nitroso-group. These results would be achieved by the change of the nitrosochloride into (XI), involving migration of the nitroso-group and a hydrogen atom, or into (XII) by interchange of hydrogen and the *gem*-dimethyl group:

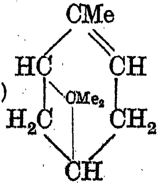


An *αγ*-change of this type is most probably involved in the formation of β- from α-dichlorocamphane under the influence of phosphorus pentachloride below 0°, and of *iso*fenchyl from fenchyl alcohol (Meerwein and Wortmann, *Annalen*, 1923, **435**, 190), and perhaps also in the generation of inactive pinol from active sobrerol by hot dilute mineral acids.

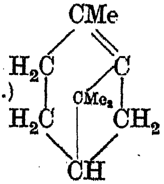
Of the alternatives (XI) and (XII), the latter is perhaps preferable, since lability of the *gem*-dimethyl group may, for the reasons already indicated, be expected to be greater than that of the nitroso-group.

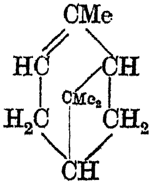
The product (XIII), derived from (XII) by elimination of the elements of nitrosyl chloride, must, according to Bredt's rule (*Ber.*, 1902, **35**, 1286), suffer a rearrangement, and this might lead either to α- or to β-pinene. But the easy conversion of β- into α-pinene by various means (Austerweil, *Bull. Soc. chim.*, 1926, **39**, 695; Delépine, *ibid.*, pp. 1475, 1479; Richter and Wolff, *Ber.*, 1926, **59**, 1733) makes it clear that the disturbed system arising from (XI) should settle down into an α-pinene. Lynn (*J. Amer. Chem. Soc.*, 1919, **41**, 361) has shown experimentally that the optically active nitrosochloride obtainable at low temperatures from active pinene reverts, on treatment with aniline, to a hydrocarbon having the same rotatory power as that originally used. The substance (XIII) can conform to this result only if interchange of the *gem*-dimethyl group and a hydrogen atom occurs. The simpler migration of a hydrogen atom would lead to the enantiomorph (XV) of the original pinene (XIV).

(XIV.)



(XIII.)





(XV.)

EXPERIMENTAL.

Action of Aniline on Trimethylethylene Nitrosochloride, m. p. 74—75°.—A solution of the nitrosochloride (3 g.) in chloroform (50 c.c.) was allowed to remain with aniline (7 g.) at the ordinary temperature for 17 hours. The resulting crystalline mass was dissolved by addition of water and more chloroform, and the anilide isolated from the chloroform solution by evaporation of the solvent at the ordinary temperature. After purification in the usual manner by solution in acetic acid and precipitation by ammonia, the crystalline product (3·7 g.) melted at 143° (Found, by micro-analysis: N, 14·3. $C_{11}H_{16}ON_2$ requires N, 14·5%).

Action of Aniline on Trimethylethylene iso*Nitrosochloride*, m. p. 48—49°.—The change of the nitrosochloride, m. p. 74—75°, to its *iso*nitroso-isomeride requires the closest adherence to the conditions prescribed by Schmidt (*Ber.*, 1902, **35**, 3734). For example, in one experiment in which stirring of the hot mass was momentarily neglected, a syrupy product insoluble in light petroleum was obtained in place of the crystalline *iso*nitroso-compound. Similar material is also gradually produced when the nitrosochloride is kept even at 0° in a stoppered bottle.

The *iso*nitrosochloride, m. p. 46—47° (0·45 g.), chloroform (5 c.c.), and aniline (0·62 g.) were allowed to react, and the product isolated, precisely in the manner just described for the nitroso-chloride. The crystalline product (0·48 g.) melted at 143° and did not depress the melting point of the above material.

Action of Aniline on the Nitrosochloride of Tetramethylethylene.—In place of the method described by Thiele (*Ber.*, 1894, **27**, 455) tetramethylethylene was prepared much more conveniently and economically by the conversion of amylene hydrate successively into trimethylethylene, its chlorohydrin, and dimethyl*iso*propylcarbinol, which was then dehydrated. Details of the procedure will be published elsewhere by one of us (J. C. E.).

(*a*) When a mixture of the nitrosochloride (2 g.), excess of aniline (6 c.c.), and alcohol (16 c.c.) was boiled under reflux, the green colour disappeared completely in 5 minutes. After a further 5 minutes, one half of the solution was cooled, treated with concentrated hydrochloric acid (6 c.c.), and kept at 0° for 2 hours. Aminoazobenzene hydrochloride (0·4 g.) was then collected and identified by liberation of the base, m. p. 119°. After crystallisation from alcohol, this, alone or mixed with authentic aminoazobenzene, melted at 124°.

An attempt to isolate the hydrocarbon from the other portion of the solution by distillation in steam was unsuccessful. Modified conditions of experiment were therefore devised for this purpose.

(*b*) A solution of the nitrosochloride (3 g.) and aniline (7 g.) in xylene (30 c.c.) was heated under reflux in boiling water for 40 minutes. By fractionation with a bead column a volatile fraction was obtained, from which, on redistillation, the hydrocarbon (1·3 c.c., b. p. 73—83°) was isolated. It was identified by conversion into the characteristic blue nitrosochloride (1·0 g.), m. p. 119—120°, which did not depress the melting point of the original material.

(*c*) A solution of the nitrosochloride (1 g.) and aniline (1·24 g.) in alcohol (15 c.c.) was divided into two equal portions. After the addition of aniline hydrochloride (0·5 g.) to one portion, both were left at the ordinary temperature for 3½ hours. Each portion then still retained a green colour, but that to which the hydrochloride had been added was perceptibly tinged with yellow. The difference in colour of the two became very much more marked when they were immersed side by side in a bath at 56—60°; after 10 minutes, the one containing the hydrochloride was orange brown, whilst the other still retained a green shade.

Action of Aniline on the Nitrosochloride of γ-Terpinyl Acetate.—The melting point of this nitrosochloride was given by Baeyer (*Ber.*, 1894, **27**, 445) as 82°, but material which had been repeatedly purified by precipitation from alcoholic solution by addition of water as recommended by Baeyer usually melted at about 77°. The discrepancy is perhaps attributable to polymerisation, since a sample which had been preserved for several weeks and again recrystallised was almost colourless and melted at 95° (Found, by micro-analysis : N, 5·2. Calc. for $C_{12}H_{20}O_3NCl$: N, 5·3%).

A mixture of the nitrosochloride (1 g.), aniline (0·36 g.), and alcohol (25 c.c.) became deep red when boiled under reflux for 35 minutes. By distillation in steam, a yellowish oil (0·5 c.c.) was isolated from which a blue nitrosochloride (0·12 g.) was obtained. This melted at 76° after precipitation from alcoholic solution by means of water, and did not depress the melting point of the original nitrosochloride.

Formation of Nitrosopinene from Pinene Nitrosochloride.—When a solution of the nitrosochloride (2 g.) in carbon tetrachloride (40 c.c.) was heated, depolymerisation was indicated by the development of a blue colour. This, however, disappeared almost immediately, presumably owing to formation of the *iso*nitroso-isomeride, and at the same time evolution of hydrogen chloride set in. After boiling for 2 minutes, the solution was cooled, and the solvent was allowed to evaporate at the ordinary temperature. By maceration of the sticky residue with ice-water, hydrochloric acid was removed. After further purification by crystallisation from light petroleum, nitrosopinene (0·38 g.), m. p. 131°, was obtained.

Pinene Nitrolanilide.—(*a*) A mixture of pinene nitrosochloride with a solution of crystallised sodium acetate (10 g.) and aniline (2·3 g.) in alcohol (150 c.c.) was boiled for 5 minutes and cooled, and excess of ice-water added. A sticky mass separated and gradually solidified. After reprecipitation by addition of ammonia to a diluted and filtered solution of the material in glacial acetic acid, it was further purified by crystallisation from light petroleum. The *anilide* was thus obtained in small, yellowish, hexagonal prisms (1·95 g.), m. p. 122° (Found, by micro-analysis : N, 10·6. $C_{16}H_{22}ON_2$ requires N, 10·8%).

(*b*) A solution of the nitrosochloride (1 g.) in chloroform (15 c.c.) was added to a mixture of aniline (0·46 g.) and pyridine (2 g.) in chloroform (5 c.c.) at 20°. After 16 hours, the solution was washed with water, dried over sodium sulphate, and allowed to evaporate at the ordinary temperature. After purification in the manner just described, the anilide (0·2 g.) was obtained crystalline, m. p. 121°, and did not depress the melting point of material prepared by the preceding method.

Diazoaminobenzene from Pinene Nitrosochloride.—As an alternative to the procedures just described, a solution of the nitrosochloride (2 g.) in chloroform (30 c.c.) was shaken with aniline

(0·92 g.) in presence of finely powdered, crystalline lead acetate (3·8 g.) at the ordinary temperature for 2½ hours. After filtering from lead chloride, the solution was allowed to evaporate at the ordinary temperature. Unchanged nitrosochloride (0·92 g.), m. p. 109—110°, remained after extraction of the residue with alcohol. The cooled alcoholic solution deposited yellow needles (0·5 g.), m. p. 79—80°, on careful dilution with water.

This material represented the labile form of diazoaminobenzene, to which Walther ascribed the melting point 79—81° (*J. pr. Chem.*, 1897, **55**, 551). The material melted at 91—92° (Found: N, 21·2. Calc.: N, 21·3%) after crystallisation from alcohol, and at 98° after further crystallisation from ligroin.

Exactly similar phenomena resulted from the use of anhydrous sodium acetate in place of lead acetate.

THE UNIVERSITY, SYDNEY. [*Received, March 16th, 1927.*]

CLXXVII.—*Researches in the Menthone Series. Part IV.* iso*Menthols and* iso*Menthones.*

By JOHN READ, GEORGE JAMES ROBERTSON, and ALISON MARY RITCHIE COOK.

OF the four possible externally compensated menthols, the two derived from *dl*-menthone—namely, *dl*-menthol (m. p. 34°) and *dl-neo*menthol (m. p. 51°)—were characterised in 1912 by Pickard and Littlebury (J., **101**, 109). Much uncertainty has existed, however, respecting the two remaining compounds, *dl-iso*menthol and *dl-neoiso*menthol, derived from *dl-iso*menthone. Bedos (*Bull. Soc. chim.*, 1926, **39**, 674) claims to have demonstrated the existence of the four racemic menthols and the two corresponding racemic menthones through a study of the interaction between magnesium *iso*propyl bromide and the two isomeric 2-chloro-5-methyl*cyclo*hexanols. This claim is open to serious criticism. In the first place, neither of the supposed new menthols was crystalline, whereas we show below that *dl-iso*menthol, prepared by the action of nitrous acid upon *dl-iso*menthylamine (J., 1926, 2232), melts at 53·5°. Secondly, the menthol prepared by Bedos from either of the above sources, or by the action of magnesium *iso*propyl bromide on the oxide of methyl-Δ^3-*cyclo*hexene, gave an inactive menthone which, from its inability to furnish crystalline derivatives, was neither pure *dl*-menthone nor *dl-iso*menthone (compare Read and Cook, J., 1925, **127**, 2783). Thirdly, the base obtained by reducing the liquid oxime of this menthone corresponded in no particular with *dl-iso*menthylamine (J., 1926, 2230).

In the present communication, we show that the mixture of menthols obtained in the reduction of *dl*-piperitone by sodium and alcohol contains *dl*-menthol as well as *dl*-*iso*menthol; the mixture is being further examined with the object of isolating the other two stereoisomerides. By the action of nitrous acid on *d*- and *l*-*iso*menthylamine, derived through *d*- and *l*-*iso*menthone from *l*- and *d*-piperitone, we have also been able to prepare *d*- and *l*-*iso*menthol. The constants for the *d*-component, m. p. 81·5°, $[\alpha]_D^{15}$ + 27·0° in alcohol, are in satisfactory agreement with the data recorded by Beckmann (*Ber.*, 1909, **42**, 846) for *d*-*iso*menthol derived ultimately from the oxime of " inverted " *l*-menthone, the values being m. p. 83°, $[\alpha]_D$ + 26·3°. Moreover, Zeitschel and Schmidt (*Ber.*, 1926, **59**, 2298) have recently recorded m. p. 85°, $[\alpha]_D$ + 23·6°, for a specimen of *d*-*iso*menthol of unspecified origin. The form of the melting-point curve of mixtures of the *d*- and *l*-modifications is that of a conglomerate. *dl*-*iso*Menthol has a melting point only slightly higher than that of *dl*-*neo*menthol, but whilst *d*- and *l*-*neo*menthol are oils the optically active *iso*menthols have a melting point 28° higher than that of the externally compensated form; *d*- and *l*-menthol also melt at a higher temperature than *dl*-menthol. These relationships, which are of particular interest in view of the apparent configurational resemblance between the menthols and the *iso*menthols (compare J., 1926, 2213), point to the possibility of *d*- and *l*-*neoiso*menthol displaying a lower melting point than *dl*-*neoiso*menthol.

The *iso*menthols now described provide the only sources at present available for the preparation of practically pure specimens of *dl*-*iso*menthone and its optically active components. Although *l*- and *d*-piperitone upon catalytic hydrogenation yield preparations of *d*- and *l*-*iso*menthone with values of $[\alpha]_D^{15°}$ as high as ± 70°, it has been pointed out in an earlier communication (J., 1926, 2211) that the optical purity of such preparations is unsatisfactory. Since Beckmann's chromic acid mixture has little inverting action on *d*-*iso*menthone (*loc. cit.*, p. 2215), it was anticipated that careful oxidation of the *iso*menthols with this reagent would furnish the corresponding *iso*menthones in a state of approximate purity. A specimen of *d*-*iso*menthone prepared in this way had $[\alpha]_D^{15°}$ + 91·7°, a value which agrees satisfactorily with $[\alpha]_D$ + 93·2°, observed by Beckmann (*loc. cit.*; compare also Barrowcliff, J., 1907, **91**, 875, and Zeitschel and Schmidt, *loc. cit.*). This ketone gives a viscid oxime, whilst the melting points recorded for the semicarbazone range from 154° (Beckmann) to 164° (Zeitschel and Schmidt). The semicarbazone prepared by us, when recrystallised once from light petroleum containing a little methyl alcohol, formed minute needles melting indefinitely at 125—138° and having $[\alpha]_{D}^{15^\circ} + 23{\cdot}8^\circ$ in absolute alcohol ($c = 1{\cdot}5$); the isolation of a homogeneous derivative from this product proved so tedious that we recommend the characterisation of *d-iso*menthone by means of the hydrochloride of the oxime, which is readily obtained in well-defined prisms, m. p. 132°, $[\alpha]_{D}^{15^\circ} + 38{\cdot}6^\circ$ in chloroform ($c = 4{\cdot}0$).

It is probable that preparations of *d*- (or *l*-)*iso*menthone made as indicated still contain a small proportion of *l*- (or *d*-)menthone, but accepting the values $[\alpha]_{D}^{15^\circ} + 91{\cdot}7^\circ$ and $[\alpha]_{D}^{20^\circ} - 29{\cdot}6^\circ$ for *d-iso*menthone and *l*-menthone, respectively, it now becomes possible to calculate with a close approximation to accuracy the composition of various equilibrium mixtures of these two readily interconvertible ketones (J., 1926, 2210). Thus, when equilibrated with alcoholic sodium ethoxide, *l*-menthone gave a mixture containing only 30% of *d-iso*menthone; this proportion rose to 37% when the ketone was maintained at 200°, and to 46% when it was treated with melting 90% sulphuric acid. Furthermore, *d*-pulegone and *l*-Δ^4-*p*-menthen-3-one, when hydrogenated in presence of colloidal palladium (*loc. cit.*), yielded mixtures containing, respectively, 52% and 60% of *d-iso*menthone; whilst the product furnished by *l*- (or *d*-)piperitone contained as much as 82% of *d*- (or *l*-)*iso*menthone, the absence of *dl*-piperitone from the preparations used being assumed.

Although the isolation of pure derivatives of *dl-iso*menthone has been described in these researches (J., 1926, 2783), it has hitherto been impossible to obtain the pure ketone, owing to the inversion which accompanies its regeneration from such derivatives. *dl-iso*Menthone may now be made, however, through the oxidation of *dl-iso*menthol; the preparation of the ketone by this method, for the purpose of determining its physical constants, is at present engaging our attention.

Owing to their method of formation, we regard the *iso*menthols as corresponding in molecular configuration to the *iso*menthylamines. In the configurational scheme recently advanced for the menthylamines (J., 1926, 2213), the *cis*- and *trans*-configurations were adopted for menthones and *iso*menthones, respectively. Measurements of the parachors (compare Sugden and Whittaker, J., 1925, **127**, 1868) recently made by Dr. P. G. Carter in this College indicate, however, that the menthones and *iso*menthones possess the *trans*- and *cis*-configurations, respectively, the mean values of $[P]$ being determined as follows: *dl*-menthone, 400·9; *l*-menthone, 403·2; *dl-iso*menthone, 405·3; *d-iso*menthone, 404·6. The calculated value for $C_{10}H_{18}O$, 1 non-polar double bond, 1 six-membered ring, is $[P]$ 405·1. The specimens of *iso*menthone used for these measurements were prepared by the catalytic hydrogenation of *dl-* and *l*-piperitone, and were thus contaminated with the corresponding menthones, as indicated above. The results agree broadly with the observations of Zeitschel and Schmidt (*loc. cit.*), who found that *d-iso*menthone gave slightly higher values for refractive index and density than *l*-menthone; the Auwers–Skita rule thus favours the *trans*-configuration for menthone, although the question cannot yet be considered as decisively settled.

EXPERIMENTAL.

dl-iso*Menthol and its Optically Active Components.*—dl-iso*Menthol.* *dl-iso*Menthylamine hydrochloride (26·6 g.), obtained by reducing *dl-iso*menthoneoxime (J., 1926, 2230), when recrystallised twice from hot acetone containing a little methyl alcohol and then treated with sodium nitrite (10 g.) in aqueous solution at 70°, yielded a partly crystalline product (14·0 g.), which was forthwith distilled in steam. A fraction (8·7 g.) of the dry material distilling at 95—100°/10 mm. and having $n_D^{16°}$ 1·4660 deposited crystalline dl-iso*menthol* (2·6 g.) at the ordinary temperature; after being kept for a few days on porous plate in a desiccator, this substance was obtained in small, glistening needles, m. p. 53·5°, with an odour similar to but considerably milder than that of *l*-menthol. The hydrochloride (33 g.) of the base formed on reducing the viscid mother-liquor from crystalline *dl*-menthoneoxime (*loc. cit.*, p. 2231) yielded a liquid mixture of menthols when treated similarly with nitrous acid; the bulk (14·5 g.) of the product distilled at 95—110°/20 mm. and had $n_D^{16°}$ 1·4660, but it proved impracticable to isolate crystalline material either from this fraction or from a refractionated portion (1·8 g.) having b. p. 97—100°/10 mm. and $n_D^{14°}$ 1·4665. dl-iso*Menthyl hydrogen phthalate*, prepared by the method of Pickard and Littlebury (J., 1912, **101**, 113), crystallised from light petroleum containing a little ether in small clusters of minute prisms, m. p. 107—108° (Found: *M*, by titration, 301. $C_{18}H_{24}O_4$ requires *M*, 304). *dl-iso*Menthol regenerated from this derivative by hydrolysis with hot alcoholic sodium hydroxide melted unchanged at 53·5°. The *hydrogen succinate* was obtained in the form of an oil which yielded a crystalline mass on cooling and seeding with the supposed *dl-iso*menthyl hydrogen succinate (m. p. 72—73°) described below; as the material was very soluble in organic solvents and available only in small amount, a satisfactory purification of this specimen could not be effected (*vide infra*). The *phenylurethane* was liquid at the ordinary temperature.

d-iso*Menthol.* Crude *d-iso*menthylamine hydrochloride (120 g.), prepared from the viscid oxime of *d-iso*menthone (J., 1926, 2221) and having $[\alpha]_D^{15^\circ}$ + 20·6° in aqueous solution, was dissolved in a hot mixture of acetone (1200 c.c.) and methyl alcohol (175 c.c.). The first two fractions to separate (40·4 g.) consisted of pure *d-iso*menthylamine hydrochloride, having $[\alpha]_D^{15^\circ}$ + 23·6° in aqueous solution (c = 2·3), whilst the residue, upon fractional crystallisation from acetone, followed by ethyl acetate, yielded a further quantity (11·8 g.) of this substance. The more soluble fractions of the material gave values of $[\alpha]_D$ ranging from + 17·2° to + 18·9° in aqueous solution.

Upon treating *d-iso*menthylamine hydrochloride (20 g.) in cold aqueous solution with the calculated amount of sodium nitrite, a crystalline separation of the nitrite of the base was obtained. The mixture was warmed to 70° and finally heated on the water-bath until the evolution of nitrogen ceased. When distilled with steam, the oily product (11·4 g.) crystallised partly in the receiver. About 15% of the original *d-iso*menthylamine was recovered unchanged. After two successive fractional distillations of material (28·8 g.) obtained in this way, the first fraction (4·9 g.) had b. p. 54—58°/12 mm., $n_D^{15^\circ}$ 1·4583, and $\alpha_D^{15^\circ}$ + 27·2° (l = 1); whilst the fourth fraction (12·4 g.), which became almost wholly crystalline, had b. p. 96—98·5°/11 mm. These fractions consisted, respectively, of approximately pure *d*-Δ^3-menthene (partly racemised) and *d-iso*menthol, and the intermediate fractions were composed of mixtures of these two substances. After purification on porous plate, d-iso*menthol* was obtained in small needles, m. p. 81·5°, $[\alpha]_D^{15^\circ}$ + 24·0° in benzene (c = 2·5), $[\alpha]_D^{15^\circ}$ + 27·0° in absolute alcohol (c = 1·8). The odour was indistinguishable from that of *dl-iso*menthol. d-iso*Menthyl hydrogen phthalate* crystallises from methyl alcohol in aggregates of small prisms, m. p. 107·5—108·5°, $[\alpha]_D^{15^\circ}$ + 27·5° in chloroform (c = 3·4). The *hydrogen succinate* was obtained as a yellowish, viscid liquid, $[\alpha]_D^{15^\circ}$ + 22·5° in chloroform (c= 3·8).

The above and other experiments indicated that *d-iso*menthylamine reacts with nitrous acid to form *d*-Δ^3-menthene and *d-iso*menthol in the approximate ratio of 1 to 2, the combined yield being about 80% of the calculated amount. Only about one-third of the *d-iso*menthol formed was actually isolated in the pure crystalline condition.

l-iso*Menthol*. *l-iso*Menthylamine hydrochloride (6 g.), prepared in the way already described (J., 1926, 2222), and having $[\alpha]_D^{15^\circ}$ — 22·6° in dilute aqueous solution, was treated with nitrous acid as described above. The fraction (0·8 g.) of the product boiling at 103—107°/19 mm. rapidly became crystalline, and when purified on porous plate yielded l-iso*menthol*, m. p. 80·5°, $[\alpha]_D^{15^\circ}$ — 24·1° in absolute alcohol (c = 1·8).

Melting-point Curve of Mixtures of d- *and* l-iso*Menthol.*—Mixtures of *d-iso*menthol (m. p. 81°) and *l-iso*menthol (m. p. 79·5—80·5°) of known compositions were prepared by direct weighing. In each case the mixture was gently fused, with stirring, the melting point being then observed in the usual way for the resolidified material. Several observations were made in each instance, and the melting points were found to be well defined and consistent. Mixtures containing 100, 89·6, 73·6, 60·1, 50·0, and 26·3% of *d-iso*menthol melted at 81·5°, 77°, 67—68°, 58—59°, 51·5°, and 65°, respectively. The corresponding melting-point curve appears to conform, within the limits of experimental error, to Roozeboom's Fig. 6 (*Z. physikal. Chem.*, 1899, **28**, 507). The observed melting point for the equimolecular mixture of *d*- and *l-iso*menthol (51·5°), which must thus be regarded as a conglomerate, agrees satisfactorily with the value recorded above for *dl-iso*menthol prepared directly from *dl-iso*menthylamine. No depression was observed in the melting point of a mixture of specimens of *dl-iso*menthol prepared in these two ways.

Preparation and Characterisation of Optically Pure d-iso*Menthone.* —*d-iso*Menthol (4 g.), m. p. 81·5°, $[\alpha]_{D}^{15°}$ + 24·0° in benzene, was added to Beckmann's chromic acid mixture at 30° (compare *Annalen*, 1889, **250**, 325). Upon shaking the mixture vigorously, the temperature rose to 50°, at which point the black chromium derivative decomposed. The resulting *d-iso*menthone was at once extracted from the cooled mixture with ether, the extract being then washed four times with water and dried over sodium sulphate. The treatment with dilute sodium hydroxide solution, adopted by Beckmann, was omitted. The crude product (3·3 g.) had $n_{D}^{16°}$ 1·4555, and represented 82·5% of the calculated yield. The first fraction (2·75 g.), distilling at 86—87°/12 mm., was regarded as pure d-iso*menthone.* It had $n_{D}^{16°}$ 1·4545, $\alpha_{D}^{15°}$ + 82·16°, $[\alpha]_{D}^{15°}$ + 91·7° (assuming $d = 0·896$; compare J., 1923, **123**, 2922). The odour was less penetrating than that of *l*-menthone.

Part of the ketone so prepared was oximated in aqueous-alcoholic solution with hydroxylamine acetate, sodium bicarbonate having been added beforehand until the solution was only faintly acid to litmus. After 3 days, d-iso*menthoneoxime* was precipitated by the addition of water and extracted with ether. When freed from the last traces of the solvent, it was obtained as a colourless, viscid oil, having $n_{D}^{17°}$ 1·4830 and $[\alpha]_{D}^{15°}$ + 45·1° in absolute alcohol ($c = 2·2$). The oil could not be induced to crystallise by applying any of the usual methods. When cooled in liquid air, either alone or in contact with light petroleum, it gave a brittle, vitreous mass, which reverted to a viscid liquid at the ordinary temperature. The p-*nitrobenzoyl* derivative is an oil. d-iso*Menthoneoxime hydrochloride*, obtained by passing dry hydrogen chloride into a cooled ethereal solution of the oxime, is the most characteristic derivative of *d-iso*menthone yet prepared. It crystallises from acetone containing a little absolute alcohol in large, transparent prisms of tabular habit, m. p. 132°, $[\alpha]_D^{15°}$ $+ 38{\cdot}6°$ in chloroform ($c = 4{\cdot}0$). With care, crystals of this substance might be characterised goniometrically. The hydrochloride reverts completely to its components in presence of water. A further purification of the oxime was therefore attempted by shaking an ethereal solution of this derivative with water containing an equivalent amount of sodium bicarbonate. After drying in a vacuum at 60°, the resulting viscid liquid had $n_D^{14°}$ 1·4865, and $[\alpha]_D^{15°}$ $+ 46{\cdot}0°$ in absolute alcohol ($c = 3{\cdot}8$).

In the course of the above characterisation of *d-iso*menthone, the following related derivatives were prepared for purposes of comparison. dl-iso*Menthoneoxime hydrochloride* crystallises from acetone in clusters of transparent prisms, m. p. 127—128° (decomp.). dl-*Menthoneoxime hydrochloride* cannot be recrystallised in the ordinary way, owing to the ease with which it is hydrolysed in presence of moisture. After being washed with anhydrous ether and dried on porous plate in a vacuum, it was obtained in minute needles, m. p. 94°. l-*Menthoneoxime hydrochloride*, purified similarly, formed long, slender prisms, m. p. 118—119°, $[\alpha]_D^{15°}$ $- 89{\cdot}1°$ in chloroform ($c = 2{\cdot}1$). The p-*nitrobenzoyl* derivative of *l*-menthoneoxime was prepared by heating equivalent amounts of the oxime and *p*-nitrobenzoyl chloride in pyridine solution on the water-bath; it separated from alcohol in pale yellow needles, m. p. 102·5°.

Attempts to prepare neoiso*Menthols and* neoiso*Menthylamines*.—1. The liquid mixture of menthols obtained by the reduction of *dl*-piperitone with sodium and absolute alcohol (J., 1925, **127**, 2784), when freed from *dl*-α-phellandrene, distilled at 90—97°/8·5 mm. and had $n_D^{15°}$ 1·4675. Treatment with phthalic anhydride (J., 1912, **101**, 113) yielded a partly crystalline mass (140 g.), which was fractionally crystallised from light petroleum, with the addition of a little absolute alcohol when necessary. The first two fractions melted at 107—112° (40 g.) and 82—87° (49 g.), respectively, whilst the residue was a viscid liquid. After three recrystallisations, the first fraction yielded large, transparent plates, which showed no alteration of melting point (131—132°) when mixed with *dl*-menthyl hydrogen phthalate. The original mixture thus contained some *dl*-menthol. The second fraction of the phthalate upon similar treatment yielded rosettes of soft needles, m. p. 93—94°, which upon hydrolysis with alcoholic sodium hydroxide yielded a menthol, m. p. 46—47°. A mixture of this preparation with pure *dl-iso*-

menthol (m. p. 53—53·5°) melted at 47—52°. The viscid fraction of the phthalate has not yet been examined further.

A specimen of crystalline menthol (m. p. 32—40°), obtained by cooling a portion of the above crude liquid menthol (b. p. 90—97°/8·5 mm.), gave a vitreous mass when heated with phthalic anhydride. Prolonged partial crystallisation from light petroleum furnished two kinds of crystals, the less soluble of which formed opaque clusters of soft needles, m. p. 103—104° (Found: C, 70·7; H, 8·3. $C_{18}H_{24}O_4$ requires C, 71·1; H, 7·9%). A more soluble series of fractions, obtained in larger amount, consisted of hard clusters of glistening prisms, m. p. 91—94° (Found: C, 70·4; H, 7·8%). Both kinds of crystals gave analytical results agreeing with those required for menthyl hydrogen phthalates, and upon hydrolysis yielded specimens of menthol melting at 46—49° and 39—42°, respectively. The corresponding mixed melting points with pure *dl-iso*menthol were 49—53° and 40—52°. The phthalate melting at 103—104° was therefore practically pure *dl-iso*menthyl hydrogen phthalate.

No definite proof of the occurrence of a third crystalline menthol in the reduction product of *dl*-piperitone is provided by the above observations. It may be added that the crude crystalline mixture of menthols, m. p. 32—40°, readily yielded a crystalline product when heated with succinic anhydride; after two recrystallisations from light petroleum, an apparently homogeneous product was isolated in small, colourless plates, m. p. 72—73°. In view of the general behaviour of the menthol from which it was derived, this substance is regarded as dl-iso*menthyl hydrogen succinate* (Found: C, 66·0; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%).

2. The mother-liquors from the recrystallisation of crude *d-iso*menthylamine hydrochloride (*vide supra*) were examined in various ways. A fraction of the hydrochloride having $[\alpha]_D$ + 18·5° (water) yielded a mixture of menthene and menthol when treated with nitrous acid. A liquid menthol fraction distilling at 93—98°/12 mm. had $n_D^{15°}$ 1·4654 and $[\alpha]_D^{15°}$ + 12·1° in benzene (c = 3·0). The corresponding partly crystalline menthol fraction furnished by pure *d-iso*menthylamine hydrochloride had $[\alpha]_D^{15°}$ + 18·5°. The acetyl derivative prepared from the same fraction of the hydrochloride was a viscid liquid having $[\alpha]_D^{15°}$ + 16·2° in chloroform. The crude salicylidene derivative had $[\alpha]_D^{15°}$ + 32·1° in chloroform (c = 5·5), m. p. 65—85°. After five recrystallisations from alcohol, the first fraction softened at 85° and melted at 107—112°, whilst the value of $[\alpha]_D^{15°}$ was + 61·1°. From these observations, it appears that the mother-liquors contained *d-iso*menthylamine, together with a lævorotatory base, and possibly also some *dl-iso*menthylamine.

3. The residual uncrystallisable syrup from the preparation of formyl-*d*-*neo*menthylamine (J., 1926, 2218) was hydrolysed with hydrochloric acid. The resulting solid mixture of hydrochlorides (69 g.) was extracted with ether in a Soxhlet apparatus in order to remove *d*-*neo*menthylamine hydrochloride. The residue (48 g.), when recrystallised from acetone containing a little methyl alcohol, gave a first fraction (10·6 g.) having $[\alpha]_{\rm D}^{15^\circ}$ — 10·7° (water), whilst a final (fourth) fraction (15·2 g.) had $[\alpha]_{\rm D}^{15^\circ}$ — 5·1°. The rotatory power of the first fraction corresponds to a mixture of 55·4% of *l*-menthylamine hydrochloride and 44·6% of *d*-*neo*menthylamine hydrochloride, it being assumed that no other base was present. This fraction, however, yielded a crude salicylidene derivative, m. p. 48°, having $[\alpha]_{\rm D}^{15^\circ}$ — 72° (chloroform). The mixture indicated above would yield a product having $[\alpha]_{\rm D}^{15^\circ}$ — 52·7°, and this would become — 34·6° if the assumed *d*-*neo*menthylamine were replaced by *d*-*iso*menthylamine. It thus appeared that a new lævorotatory salicylidene derivative must be present in the product derived from the first fraction of the hydrochloride. Similar results were obtained with the succeeding fractions, and eventually, after recrystallising the crude salicylidene derivative three times from light petroleum, a homogeneous product was obtained, having m. p. 99—100°, $[\alpha]_{\rm D}^{15^\circ}$ — 17·9° (chloroform). This substance appears to be the salicylidene derivative of an active form of the hitherto unknown *neoiso*menthylamine (compare J., 1926, 2213, 2225), which base we hope to isolate and characterise in continuing our researches on menthylamines.

The authors are indebted to the Carnegie Trust for a Teaching Fellowship and a Scholarship which enabled two of them (G. J. R. and A. M. R. C.) to take part in the work; their thanks are also due to Dr. F. G. Mann, of the University Chemical Laboratory, Cambridge, for his kindness in examining the effect of liquid air on *d*-*iso*menthoneoxime.

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[*Received, April 5th*, 1927.]

CLXXVIII.—*A Method for the Estimation of Small Quantities of Water in Alcohol.*

By ERNEST LESTER SMITH.

THE methods at present available for the determination of water in alcohol may be divided into two groups: (1) physical methods, comprising the density method and methods depending on the effect of water on the miscibility of certain liquids with alcohol, such as Crismer's kerosene method (*Bull. Soc. chim. Belg.*, 1904, **18**, 18; also Curtis, *J. Physical Chem.*, 1898, **2**, 371; Nussbaum, *J. Pharm. Chim.*, 1917, **15**, 230; Jones and Lapworth, J., 1914, **105**, 1804); (2) chemical methods depending on the interaction of the water with substances such as calcium hydride (Worth, *Z. Deut. Oel-Fett Ind.*, 1921, **41**, 147), or calcium carbide (Newman, *J. Soc. Chem. Ind.*, 1924, **43**, 285; also Weaver, *J. Amer. Chem. Soc.*, 1914, **36**, 2462; Hartley and Raikes, J., 1925, **127**, 526). The accuracy claimed for the majority of these processes is not greater than 0·03 unit in the percentage of water. A further disadvantage inherent in nearly all the methods is the necessity for calibration with standard alcohol–water mixtures, the preparation of which is a matter of extreme difficulty where very small percentages of water are concerned.

In view of these considerations, an attempt was made to devise a new method. When the sodium or potassium compound of a hydroxylic substance such as phenol or alcohol is dissolved in aqueous alcohol, it is partly hydrolysed with formation of sodium or potassium hydroxide, an equilibrium being set up. If an ester is present, it will be hydrolysed irreversibly by the free alkali; the equilibrium is thereby disturbed and the reaction proceeds until either the alkali compound, the ester, or the water disappears completely. Provided that the concentration of the water is less than that of the other reactants, conditions can be so chosen that the reaction approaches completion with respect to this component in a relatively short time. It is possible by means of an extrapolation method to find the "limiting titration," *i.e.*, the titre at infinite time, and the difference between this and the initial titration is equivalent to the water concentration. Sodium or potassium ethoxide is employed, prepared by dissolving the metal in the alcohol to be tested, and ethyl acetate as the ester.

EXPERIMENTAL.

In carrying out the estimation, it is essential to use perfectly dry apparatus, and to reduce the manipulation of the solutions to the minimum, so as to avoid exposure to the air for more than a few seconds. Hard glass tubes of about 13 c.c. capacity are used as reaction vessels, and are closed with corks soaked in paraffin wax just before use and tied down with string. Finally, the tubes are inverted and dipped into molten paraffin wax for a few seconds, which effectually protects the contents against the possible entrance of water.

Sodium or potassium may be used; if the former, sodium acetate crystallises in the tubes. This solid does not appear to affect the results, however, the same value being obtained whichever metal is employed.

The solution is prepared as follows : A quantity of the alcohol to be tested (40 to 80 c.c.) is poured into a small, dry, narrow-necked flask. A clean piece of sodium or potassium, large enough to make the solution about $N/2$, is cut under the surface of the oil in which it is kept, and rapidly transferred to the alcohol, without removal of the oil film from the surface of the metal, which is therefore not exposed to the air at all. The trace of oil does not interfere with the estimation. The metal is allowed to dissolve, the flask being closed by a calcium chloride tube and, if necessary, cooled in water. A few c.c. of ethyl acetate (dried over sodium) are now added, and immediately 10 c.c. of the solution are withdrawn by means of a dry pipette, and titrated rapidly. The pipette is fitted with a trap, consisting of a narrow glass tube bent into a loop, and filled with fine granules of calcium chloride, to prevent moisture from the mouth finding its way into the solution. This is next delivered into the tubes with the same pipette, care being taken to replace the cork as soon as a tube is charged. When ready, the tubes are sealed with wax as described, and placed in a bath of water at about 70°. The water is covered with oil to prevent steam arising, and the tubes are supported in a rack so that the corks are not below the surface of the water. In practice, a thermostat was used, but this is not essential. After 10 to 30 minutes, tubes are withdrawn at intervals and cooled in water, and the contents are titrated. It should be found that successive titration values are constant or decrease slightly. In the latter case, the extrapolation method described below must be applied to find the "limiting titration." The difference between the initial and the limiting titration corresponds to the water in the alcohol. If $N/8$-acid is used, this difference, in c.c., multiplied by the factor 0·0225 gives the percentage of water by volume directly.

It is occasionally found that one (or more) of the tubes gives an abnormally low titre, owing to the introduction of a trace of water. Such a reading may be neglected. When the amount of ethyl acetate added exceeds about 1 c.c., the volumes of ester and alcohol are measured approximately and allowance is made for the slight increase in the volume of the solution on addition of the ester. It is assumed that the addition of the alkali metal does not alter the volume.

Two methods have been used for finding the "limiting titration" : (1) the titrations are plotted against time, and the slope of the curve at various points is calculated. The slopes are then plotted against the corresponding titration values, yielding a nearly straight line which can be extrapolated to zero slope, and the "limiting titration" read off; (2) the titrations are plotted against the reciprocal of the time, giving a similar curve which can be extrapolated to zero 1/Time in the same way. The two methods agree well, the values for percentage of water not differing by more than 0·004%. The second is the simpler and more trustworthy and was used in most cases.

A further modification, which was developed towards the end of the research, allows of still greater simplification. It consists in using a considerable excess of potassium or sodium, and also of ethyl acetate, so that, when the water has nearly disappeared, the concentrations of ethoxide and ester are still large ($N/4$ to $N/2$).

Under these conditions, the reaction is extremely rapid, and proceeds to completion, as nearly as can be estimated, in 10 to 40 minutes at 70°. Thus there is no necessity for extrapolation, and also less material is required, for it is only necessary to take sufficient for two or three tubes, the contents of which are titrated after ½ hour or 1 hour, and should, of course, give the same titration value. Moreover it is not necessary to heat the tubes in a thermostat, since a constant temperature is not necessary. In this form, the method may be described as an indirect titration of water with standard acid. The process is extremely delicate and the accuracy attainable is limited, not by lack of sensitiveness, but by the difficulty of preventing the entry of further traces of moisture into the alcohol during the course of the estimation.

Results.—The following experiments are typical, the first of a case where extrapolation had to be applied, and the second of a case where this was unnecessary.

Sample D.

Sodium used. Water added, 0·335%. Ester volume correction, 3%.

Time (mins.) ...	0	5	10	23	35	58	92	155	∞
Titre ($N/8$-acid)	28·3	14·1	11·4	9·7	9·3	9·05	8·8	8·7	8·6

Diff. = 28·3 − 8·6 = 19·7 c.c.

% Water = 19·7 × 0·0225 × 1·03 = 0·457%.

Sample F.

Potassium used. No water added. Ester volume correction, 5%.

Time	0	10	43	63	113
Titre ($N/4$-acid).........	15·55	13·25	13·2	13·2	13·2

Diff. = 15·55 − 13·2 = 2·35 c.c.

% Water = 2·35 × 0·045 × 1·05 = 0·111%.

The degree of accuracy attainable in this estimation was only to be arrived at by repeating it several times with the same sample of alcohol. A further check could be obtained by adding a known quantity of water and estimating the total amount present.

The following results have been obtained :

Sample D.

Expt.	% H_2O added.	% H_2O found.	% H_2O originally in alcohol.
1	—	0·117	0·117
2	—	0·122	0·122
3	0·335	0·457	0·122

Sample H.

Expt.	1	2	3
% H_2O in alcohol	0·151	0·162	0·157

Sample I.

Expt.	% H_2O added.	% H_2O found.	% H_2O originally in alcohol.
1	—	0·022	0·022
2	0·158	0·164	0·006
3	0·164	0·176	0·012
4	0·218	0·229	0·011

These results show that it is possible to estimate the water in alcohol by this process to 0·01%. This is, therefore, one of the most accurate processes yet devised for the estimation of small quantities of water in alcohol, and also one of the simplest if the final modification is employed. Moreover, it possesses one outstanding advantage over almost every other method in that the result can be calculated directly from the readings obtained and there is no necessity for calibration against alcohol–water mixtures of known composition.

The author wishes to express his thanks to Dr. Crocker for the great interest he has taken in this research, and to the London County Council for a grant which enabled the work to be undertaken.

CHELSEA POLYTECHNIC. [*Received, April 4th*, 1927.]

CLXXIX.—*A Process for the Dehydration of Alcohol.*

By ERNEST LESTER SMITH.

SINCE the water present in alcohol is very completely consumed in the estimation process described in the preceding paper, it seemed possible that the reaction might be utilised as a method of dehydrating alcohol. Dry ethyl alcohol is a very hygroscopic substance from which it is difficult to remove the last traces of water. The ideal process would be to employ a rapid, irreversible, and preferably homogeneous reaction in which the water is consumed; also the dehydrating agent and the products of the reaction should be non-volatile so that the alcohol may be distilled off uncontaminated. This ideal is not attained completely by any of the methods in use at present for the preparation of anhydrous alcohol.

The reaction between sodium or potassium ethoxide, an ester, and water in alcohol approaches very close to the ideal suggested, in respect of rapidity, irreversibility and homogeneity. The reactants and products are all non-volatile with the exception of the ester. This difficulty, however, can be surmounted by the use of an ester of high boiling point such as ethyl succinate, from which the alcohol can be separated by fractional distillation. The process evolved is as follows: The alcohol to be dehydrated is contained in a flask, fitted with a fractionating column, attached to a condenser which can be used either for refluxing or for distillation, without disconnexion. The requisite amount of sodium is dissolved in the alcohol, and the corresponding quantity of ethyl succinate added. The mixture is refluxed for about 2 hours and then distilled, the condenser being closed by a calcium chloride tube to prevent the entrance of moisture.

25 Grams of ethyl succinate and 7 g. of sodium suffice to remove 0·5% of water from a litre of alcohol, and scarcely any loss of alcohol occurs. It is well to use approximately the above quantities even when the water present is much less than 0·5%, so that a considerable excess of the "dehydrating agents" remain, and the water is rapidly consumed. The residue can be used to dry a further smaller quantity of alcohol. An attempt has been made to estimate the amount of water in samples of this "super-dry" alcohol by the method described in the previous paper. The results, however, are indicative rather of the slight imperfections in the estimation process than of the true amount of water in this alcohol, which is too small to be estimated accurately by any known method. The mean of three such estimations was 0·01%. It is highly probable, especially in view of the enhanced hygroscopic nature of extremely dry alcohol, that the greater part of this water found its way into the alcohol during the estimation.

There remain two criticisms which may be levelled at this process for the preparation of anhydrous alcohol: (1) a certain amount of the ester may distil over with the alcohol; (2) the ethoxide and the ester may react directly to form ethyl ether, which also would contaminate the product. These will be dealt with in turn.

It was considered unlikely that ethyl succinate would be carried over with the alcohol, owing to its high boiling point (216·5°), and a very short fractionating column was used. The alcohol, when tested, however, was found to contain 0·04 g. of ester per litre.

This impurity could probably be removed by the use of a more efficient fractionating column.

The second possibility was suggested by Cashmore, McCombie, and Scarborough (J., 1921, **119**, 970) to explain the fact that esters react with potassium ethoxide in "dry" alcohol. They state "the quantity (of ether) formed would be too small to detect." The present work renders it certain that the main reaction in their case was due to the water present in the "dry" alcohol used, since even at 70° no measurable reaction occurs after the water has disappeared. If ether were formed, of course, the titres would decrease.

This point was subjected to a more rigorous test by carrying out the reaction in concentrated solutions at 100° in sealed tubes. The titres remained constant within the limits of experimental error over a period of 11 hours. It can be safely asserted that the suggested reaction does not take place to a measurable extent, if at all, even under the above conditions, and that no ether will be formed in the dehydration of alcohol by the method described above.

From all points of view, this process is exceedingly efficient for the thorough dehydration of alcohol.

The author desires to record his appreciation of the interest which Dr. Crocker has taken in the progress of this research, and to thank the London County Council for a grant which enabled it to be undertaken.

CHELSEA POLYTECHNIC. [*Received, April 4th*, 1927.]

CLXXX.—*Acid and Salt Effects in Catalysed Reactions. Part IX. A General Kinetic Method for the Determination of the Degree of Dissociation of Water.*

By HARRY MEDFORTH DAWSON.

IN Part VIII of this series of papers (this vol., p. 1146) it was shown that the coefficients k_h and k_{OH}, which represent respectively the catalytic activities of the hydrogen and hydroxyl ions, may be derived from the reaction velocity and the hydrogen-ion concentration which are characteristic of the isocatalytic point on the H^+–OH^- catenary.

On the assumption that the catalysed hydrolytic reactions in question are such that the effect of the undissociated water molecules may be neglected, the isocatalytic data are given by the equations

$$[H^+]_i = \sqrt{k_{OH}K_w/k_h} \text{ (1) and } v_i = 2\sqrt{k_h k_{OH} K_w} \quad . \quad . \quad (2)$$

If the ionisation constant, K_w, of the solvent is unknown, it is apparent that these equations afford a means of determining it. Three methods of procedure are possible, for by the combination of equations (1) and (2) we obtain

$$K_w = k_h[\mathrm{H}^+]_i^2/k_{\mathrm{OH}} \quad \ldots \quad (3)$$

$$K_w = [\mathrm{H}^+]_i v_i/2k_{\mathrm{OH}} \quad \ldots \quad (4)$$

and

$$K_w = v_i^2/4k_h k_{\mathrm{OH}} \quad \ldots \quad (5)$$

These equations involve three of the four possible ternary combinations of k_h, k_{OH}, $[\mathrm{H}^+]_i$, and v_i, and it should be noted that they all presume a knowledge of k_{OH}. The fourth combination (k_h, $[\mathrm{H}^+]_i$, and v_i) does not provide a means of determining K_w, and this is due to the circumstance that these three quantities are uniquely connected by the relation $v_i = 2k_h[\mathrm{H}^+]_i$.

In the application of the methods suggested by the above equations, it should be noted that the determination of the isocatalytic data corresponding with the joint effect of the hydrogen and hydroxyl ions usually requires the stabilisation of the p_{H} value at which the velocity is measured, and this may, of course, be effected by the employment of buffer mixtures. Apart from the displacement of the isocatalytic point of the H^+–OH^- catenary by the acid and salt constituents of the buffer mixture (compare Dawson, Part VIII), there are various other points to be considered which have a direct bearing on the determination of the isocatalytic data in buffered solutions, and also on the differentiation between equations (3), (4), and (5) as a means of obtaining K_w. These are of particular importance when, as is frequently the case, the products of the hydrolytic change are acidic or basic, and thus tend to alter the p_{H} value of the medium in which the reaction is taking place.

For the sake of simplicity it may be supposed that the catalysed reaction is the hydrolysis of an ester of the acid HA, and that the p_{H} value is stabilised by a mixture of HA and the corresponding salt. If x is the ratio of acid to salt in the buffer mixture, the p_{H} value is given by $p_{\mathrm{H}} = \log 1/K - \log x$. If, further, the smallest possible change of x which permits of the measurement of the reaction velocity is denoted by Δx, it follows that $\Delta p_{\mathrm{H}}/\Delta x = -1/2{\cdot}3x$, or that the resulting change in the p_{H} value of the solution is inversely proportional to the acid–salt ratio of the buffer mixture. This consideration shows that buffer mixtures with a low acid–salt ratio are not generally suitable for use in the measurement of reaction velocities.

Furthermore, since the rate of change of the reaction velocity with change of p_{H} approximates to zero in the neighbourhood of the isocatalytic point, whilst $\Delta p_{\mathrm{H}}/\Delta v$ attains its highest values in this region, it is apparent that the minimum velocity can in general be determined with much greater accuracy than that which is associated with the determination of the hydrogen-ion concentration characteristic of the isocatalytic point. For this reason, it would appear that equation (5) is very much to be preferred to equations (3) and (4) as the basis of a method for the determination of K_w.

It is scarcely necessary to add that the absolute concentration of the buffer mixture should be as small as is consistent with the adequate stabilisation of the hydrogen-ion concentration. Less obvious is the circumstance that the mode of making up the series of buffer solutions is of considerable importance. The p_H value is determined by K and by the acid–salt ratio, but of the various possible ways in which the acid and salt may be mixed together to produce a series of buffer mixtures with the required range of p_H values, there are two sets of combinations which are unique in the sense that the mathematical treatment of the catalytic relations which are associated with their use is relatively very simple. The two sets of buffer mixtures referred to are those for which (1) the concentration (c) of the acid or (2) that (s) of the salt is kept constant.

These two series of buffer mixtures give isocatalytic points, the p_H values of which are, in general, less and greater, respectively, than the corresponding p_H value for the H^+–OH^- catenary. The isocatalytic data $[H^+]_i$ and v_i for this catenary are given by equations (1) and (2). For the constant-acid series of buffer mixtures it has already been shown (Dawson, *loc. cit.*, p. 1149) that the corresponding data $[H^+]_i'$ and v_i' are given by

$$[H^+]_i' = \sqrt{(k_aKc + k_{OH}K_w)/k_h} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$v_i' = 2\sqrt{k_h(k_aKc + k_{OH}K_w)} + k_mc \quad . \quad . \quad . \quad (7)$$

By proceeding in a similar manner, it is possible to derive expressions for the isocatalytic data $[H^+]_i''$ and v_i'' for a series of buffer solutions of the type cHA + sMA in which the salt concentration (s) is kept constant. Certain restrictions are in this case necessary, and it will be assumed that the acid is relatively weak, that the hydrogen-ion concentration is given by $[H^+] = Kc/s$, and that k_m can be neglected in comparison with k_h.

The general equation

$$v = k_h[H^+] + k_{OH}[OH^-] + k_a[A^-] + k_m[HA]$$

may then be written :

$$v = k_h[H^+] + k_{OH}K_w/[H^+] + k_as + k_mc$$

whence

$$v = (k_h + k_ms/K)[H^+] + k_{OH}K_w/[H^+] + k_as.$$

Differentiation of this equation shows that the reaction velocity passes through a minimum when

$$[\mathrm{H}^+] = [\mathrm{H}^+]_i'' = \sqrt{k_{\mathrm{OH}}K_w/(k_h + k_m s/K)} \quad . \quad . \quad . \quad (8)$$

By substitution of this in the previous equation, we obtain :

$$v_i'' = 2\sqrt{(k_h + k_m s/K)k_{\mathrm{OH}}K_w} + k_a s \quad . \quad . \quad . \quad (9)$$

Equations (8) and (9) express relations which are thus applicable to the isocatalytic points indicated by experiments with buffer solutions of constant salt concentration (s).

In order to illustrate the numerical differences which are involved in the use of such buffer solutions, we may compare the isocatalytic data for the acetone–iodine reaction without buffer, and the corresponding data with acetate buffers of constant-acid and of constant-salt concentration. Table I shows the values of p_{H} at which the reaction velocity is a minimum, the minimum ionic reaction velocity (u_i), and the minimum total velocity (v_i).

TABLE I.

Isocatalytic data with and without buffer mixtures.

Buffer mixture.	$(p_{\mathrm{H}})_i$.	u_i.	v_i.
None	4·68	1·94	1·94
Acetate buffer, $c = 0{\cdot}01$	4·33	4·38	5·88
Acetate buffer, $s = 0{\cdot}01$	4·90	1·16	5·66

It is apparent that the isocatalytic data for the two series of buffer solutions differ very widely from the data which are really characteristic of the H^+–OH^- catenary. The wide deviation in this case is due to the relatively large magnitude of the ratios k_a/k_h and k_m/k_h for the acetone–iodine reaction, and it may be anticipated that the differences in question will not be so pronounced when other hydrolytic reactions are considered.

The minimum velocity, v_i, characteristic of the H^+–OH^- catenary may be derived from the minimum velocity v_i' obtained with buffers of constant acid concentration by combining equations (2) and (7), and from the minimum velocity v_i'' observed with buffers of constant salt concentration by the combination of (3) and (9).

From (2) and (7) we obtain

$$v_i = (v_i' - k_m c)/\sqrt{(1 + k_a Kc/k_{\mathrm{OH}}K_w)} \quad . \quad . \quad . \quad (10)$$

and from (3) and (9)

$$v_i = (v_i'' - k_a s)/\sqrt{(1 + k_m s/Kk_h)} \quad . \quad . \quad . \quad . \quad (11)$$

If the disturbances due to the buffer mixtures are inconsiderable, as in the case when c and s are small, it may be shown that equation (10) reduces to the form

$$v_i = v_i' - k_m c - k_a s' \quad . \quad . \quad . \quad . \quad . \quad (10\mathrm{A})$$

where s' is the salt concentration at which minimum velocity is observed with buffers of constant acid concentration c.

Similarly, equation (11) assumes the form

$$v_i = v_i'' - k_a s - k_m c' \quad . \quad . \quad . \quad . \quad . \qquad (11\text{A})$$

where c' represents the acid concentration at which minimum velocity is found with buffers of constant salt concentration s.

Having thus shown how the minimum reaction velocity v_i may be derived from observations made with buffered solutions, we may proceed to the derivation of K_w on the basis of equation (5).

Dissociation Constant of Water at 25°.

The experimental data employed in the calculation of K_w have reference to the rate of hydrolysis of ethyl acetate.

It will be assumed that k_h is given by the rate of hydrolysis in the presence of dilute hydrochloric acid. According to the data compiled by Schreiner (*Z. anorg. Chem.*, 1921, **116**, 102), the ratio v/c is very nearly constant for values of c between 0·025 and 0·25 mol. per litre. The value adopted here is $k_h = 6{\cdot}45 \times 10^{-3}$ (time in minutes).

Measurements by Arrhenius of the rate of saponification of ethyl acetate (*Z. physikal. Chem.*, 1887, **1**, 110) give $k_{OH} = 6{\cdot}58$ at 24·7°, which corresponds with $k_{OH} = 6{\cdot}70$ at 25°. The data obtained by Warder (*Ber.*, 1881, **14**, 1361) and Reicher (*Annalen*, 1885, **228**, 257) lead to $k_{OH} = 6{\cdot}30$ at 25°. For the purpose of this paper, the mean value, $k_{OH} = 6{\cdot}50$, is taken.

Karlsson (*Z. anorg. Chem.*, 1925, **145**, 1) has recently determined the rate of hydrolysis of the ester in acetate buffers of constant salt concentration (0·02 mol. of sodium acetate per litre), and gives for $k = 1/t \,.\, \log_{10} c_0/c$ a minimum value of $0{\cdot}24 \times 10^{-7}$. This, when multiplied by 2·30, gives $0{\cdot}55 \times 10^{-7}$, which is taken as a measure of v_i''.

The other quantities required are k_a and k_m, and these have been furnished by systematic experiments on the hydrolysis of ethyl acetate under the catalytic influence of mixtures of the series $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + xN\text{-}CH_3{\cdot}CO_2Na$. These experiments, which will be described in a later paper, give $k_a = 2{\cdot}00 \times 10^{-7}$ and $k_m = 14{\cdot}0 \times 10^{-7}$.

By substitution in equation (11) we obtain :

$$v_i = (0{\cdot}55 \times 10^{-7} - 2 \times 0{\cdot}02 \times 10^{-7})/\sqrt{1 + (14 \times 10^{-7} \times 0{\cdot}02)/1{\cdot}85 \times 10^{-5} \times 6{\cdot}45 \times 10^{-3}}$$

$$= (0{\cdot}51/\sqrt{1{\cdot}235})10^{-7} = 0{\cdot}46 \times 10^{-7}$$

Inserting this value of v_i in equation (5) we have :

$$K_w = (0{\cdot}46 \times 10^{-7})^2/4 \times 6{\cdot}45 \times 10^{-3} \times 6{\cdot}5$$
$$= 1{\cdot}25 \times 10^{-14}.$$

The value of K_w obtained by this kinetic method depends primarily on the degree of accuracy of the measurement of v_i'' in the experiments with the buffer solutions, but there seems to be no reason why such measurements should not be made with very considerable accuracy.

It may be noted that $K_w = 1{\cdot}25 \times 10^{-14}$ is not far removed from the mean of those recorded in the Landolt–Börnstein–Roth tables. With the exception of Kanolt's value of $0{\cdot}82 \times 10^{-14}$ (*J. Amer. Chem. Soc.*, 1907, **29**, 1414), the indexed figures fall between $1{\cdot}04 \times 10^{-14}$ and $1{\cdot}42 \times 10^{-14}$. The latter values are derived on the assumptions of the classical theory, and any close comparison would necessitate a re-examination of the data from the standpoint of the modern view that the strong electrolytes are for practical purposes completely ionised.

A point of considerable interest is involved in the use of the above value of K_w for the calculation of the minimum velocity v_i from equation (2).

This gives

$$v_i = 2\sqrt{6{\cdot}45 \times 10^{-3} \times 6{\cdot}5 \times 1{\cdot}25 \times 10^{-14}} = 0{\cdot}46 \times 10^{-7}$$

which is identical with the velocity derived from equation (11). The close agreement of the observed minimum velocity when corrected for the catalytic effects of the buffer mixture with the velocity calculated from equation (2) is very significant. It would at least appear to afford substantial evidence in favour of the general accuracy of the kinetic method which has been described.

The Dissociation Constant of Water at Higher Temperatures.

In a series of experiments carried out in quartz tubes, Karlsson (*Z. anorg. Chem.*, 1921, **119**, 69) has determined the minimum rate of hydrolysis of ethyl acetate in acetate buffers of constant salt concentration (0·02 mol. per litre) at 85·5°. The minimum velocity so obtained will be utilised here for the derivation of K_w at 85·5°.

It is to be noted that the values of k_h and k_{OH} cannot be obtained by direct observations at this temperature. Within the range at which direct measurement is possible, both coefficients have been determined at a series of temperatures, and it has been shown that in both cases the influence of temperature on the velocity coefficient can be accurately represented by the Arrhenius formula

$$\log_e k'/k = A(1/T - 1/T').$$

This equation has consequently been utilised to obtain the required values of k_h and k_{OH} at 85·5°.

The value of k_h for 25°, in combination with the velocity coefficients for dilute hydrochloric acid at 20° (Poma, *Medd. Vetenskaps. Nobelinst.*, 1912, 2, No. 11) and at 35° (Karlsson, *loc. cit.*), gives $A = 8440$, and from this the value $k_h = 0{\cdot}770$ at 85·5° is obtained.

The measurements of Warder and of Reicher (*loc. cit.*) over the range 0—40° give $A = 5578$, from which $k_{OH} = 148{\cdot}7$ at 85·5°. Karlsson's value for $k = 1/t \,.\, \log_{10} c_0/c$ is 68×10^{-7}, and this, when multiplied by 2·30, gives $v_i'' = 156 \times 10^{-7}$.

The coefficients k_a and k_m required for the buffer correction in accordance with equation (11) are not available, but as a first approximation it may be assumed that the relative effect of the buffer on the minimum velocity is the same at 85·5° as at 25°. According to this, $v_i = 46/55\, v_i'' = 0{\cdot}835\, v_i'' = 130 \times 10^{-7}$. Inserting this value of v_i in equation (5), we obtain $K_w = 37 \times 10^{-14}$.

The chief objection to the above assumption is involved in the decrease in the value of the dissociation constant K of acetic acid with rise of temperature. By interpolation from the recorded values at 25°, 100°, and 156°, we obtain $K = 1{\cdot}25 \times 10^{-5}$ at 85·5°, and when this correction is introduced, the relation between v_i and v_i'' becomes $v_i = 0{\cdot}80\, v_i''$ and the value of $K_w = 34 \times 10^{-14}$.

There are two recorded series of measurements of K_w at high temperatures with which the above value may be compared. Lorenz and Böhi (*Z. physikal. Chem.*, 1909, **66**, 733) have derived values between 0° and 100° from measurements of the *E.M.F.* of the cell $0{\cdot}1N\text{-HCl}|0{\cdot}1N\text{-KCl}|0{\cdot}1N\text{-KOH}$, whilst Noyes, Kato, and Sosman (*ibid.*, 1910, **73**, 1) base their values for 100°, 156°, 218°, and 306° on conductivity data obtained in connexion with the determination of the degree of hydrolysis of ammonium acetate.

Since the heat of ionisation of water varies very considerably with the temperature, the plot of $\log K_w$ against $1/T$ does not give a straight line, but the curvature of the plot is so small that there is no difficulty in estimating the value of K_w at 85·5°. For the *E.M.F.* data, the graph gives $K_w = 44 \times 10^{-14}$, whilst the hydrolytic measurements lead to $K_w = 28 \times 10^{-14}$.

The value $K_w = 34 \times 10^{-14}$ afforded by the kinetic method described in this paper thus lies between the two values which have been previously put forward. This again may be regarded as evidence in support of the belief that the determination of the minimum reaction velocity of hydrolytic reactions under the stabilised p_H conditions which are afforded by the use of buffer solutions, provides a method for the determination of the degree of dissociation of water which should yield results of considerable accuracy. With the description and illustration of the method, the main object of this paper has been attained, and until further observations are made, it is obviously not possible to discuss in detail the merits of the kinetic method in relation to those of previous methods.

Summary.

A general kinetic method for the determination of the dissociation constant of water is described.

In accordance with the equation $K_w = v_i^2/4k_hk_{OH}$, the method involves the determination of k_h and k_{OH} and of the minimum velocity v_i, which is characteristic of the H^+–OH^- catenary.

The value of v_i is derived from measurements of the minimum reaction velocity in buffer solutions of constant acid or constant salt concentration.

For temperatures at which the coefficients k_h and k_{OH} cannot be directly measured, the required values are obtained by the use of the Arrhenius formula.

From Karlsson's measurements of the minimum speed at which ethyl acetate is hydrolysed in acetate buffers, the values derived for K_w are $1{\cdot}25 \times 10^{-14}$ at 25° and 34×10^{-14} at 85·5°.

The acid and salt effects associated with the use of buffer solutions for the stabilisation of p_H in reaction velocity measurements are discussed.

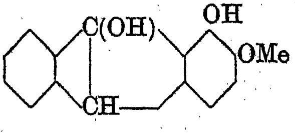
THE UNIVERSITY, LEEDS. [*Received, April 21st*, 1927.]

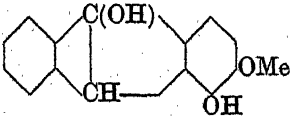
CLXXXI.—*Reduction Products of the Hydroxyanthraquinones. Part VIII.*

By EDWIN JOHN CROSS and ARTHUR GEORGE PERKIN.

WHEN unsymmetrical hydroxyanthraquinones are reduced to hydroxyanthranols, two isomerides can theoretically be obtained; for example, alizarin 2-methyl ether, by treatment with stannous chloride and hydrochloric acid (Miller and Perkin, J., 1925, **127**, 2684), gives both 1-hydroxy-2-methoxy- (I) and 4-hydroxy-3-methoxy-anthranol (II), the former in larger amount. As a rule, however, only one isomeride is produced by the reduction; thus 1- and

(I.)



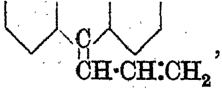


(II.)

2-hydroxyanthraquinones yield 1- and 3-hydroxyanthranols, respectively, the theoretically possible isomerides not being produced. The position of the hydroxyl in a hydroxyanthranol therefore cannot be predicted.

The positions of the hydroxyls in the anthranols of anthragallol, anthra-, and flavo-purpurins have now been studied by the method employed by one of us in earlier work and by Miller and Perkin (*loc. cit.*), *viz.*, the conversion of the hydroxyanthranol into the hydroxybenzanthrone, followed by a study of the behaviour of the product when methylated with methyl iodide and alkali. Bistrzycki and Yssel de Schepper (*Ber.*, 1898, **31**, 2790) obtained a 3 : 4 : 7-trimethoxyanthrone (which when oxidised gives flavopurpurin trimethyl ether) by the action of sulphuric acid on 4′ : 5 : 6-trimethoxydiphenylmethanecarboxylic acid, but there is no evidence that this is a methylation product of the hydroxyanthranol derived from flavopurpurin itself (Liebermann, *Ber.*, 1888, **21**, 435).

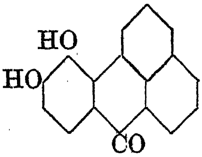
A drawback to the application of the benzanthrone process (employing glycerol and sulphuric acid) to the hydroxyanthranols is that these are more or less decomposed by the sulphuric acid before the desired reaction occurs, and so the yield of hydroxybenzanthrone is sometimes very small or even infinitesimal. The replacement of sulphuric acid by potassium hydrogen sulphate is sometimes effective. As a rule, more certain results can be obtained by passing hydrogen chloride through a mixture of the hydroxyanthranol and acraldehyde in acetic acid solution. For example, although hydroxybenzanthrones could be prepared in satisfactory amount from the anthranols of anthrapurpurin and anthragallol by all three methods, the acraldehyde method alone was successful in the conversion of flavopurpurin-anthranol into the trihydroxybenzanthrone. 3-Hydroxyanthranol thus gives 2-hydroxybenzanthrone. By this method, however, benzalizarin could not be obtained from 3 : 4-dihydroxy(alizarin)-anthranol.

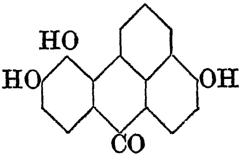
The preparation of hydroxybenzanthrone derivatives by the direct action of acraldehyde in this manner is interesting, because in order that ring formation may take place from the allylanthranol, 

, which is evidently the first product of the reaction, an oxidising agent is necessary. This is presumably supplied by the excess of acraldehyde present, which, as the result, is reduced to allyl alcohol.

The hydroxybenzanthrone, $C_{17}H_{10}O_4$, derived from anthrapurpurin-anthranol closely resembles benzalizarin (III) in properties. Since it yields a *triacetyl* derivative on acetylation, and with methyl iodide and alkali in theoretical amount a *trimethyl ether*, it is evidently the 2 : 7 : 8-trihydroxy-compound (IV).

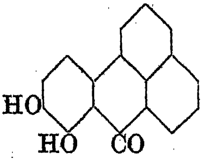
(III.)



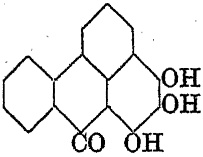


(IV.)

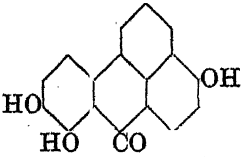
This substance, which we have named *benzanthrapurpurin*, gives a crimson oxonium salt, $C_{17}H_{10}O_4,H_2SO_4$, and dyes shades similar to, although slightly yellower than, those given by anthrapurpurin itself. On the other hand, iso*benzanthragallol*, $C_{17}H_{10}O_4$, obtained in a similar manner from anthragallol-anthranol, crystallises in yellow needles and differs markedly from anthragallol in properties. On acetylation, a *diacetyl* compound only is obtained, and the substance is not methylated by treatment with methyl iodide or with methyl sulphate and alkali. With diazomethane, however, a *dimethyl ether* is produced. This is unattacked by prolonged boiling with acetic anhydride and pyridine, but gives with alcoholic potash a *potassium* salt, and it is thus evident that of the three hydroxyls present in this compound one, evidently adjacent to a carbonyl group, is remarkably resistant both to methylation and to acetylation. A somewhat similar difficulty was experienced in the case of *iso*benzalizarin (V) (*loc. cit.*). *iso*Benzanthragallol is consequently either a 2 : 3 : 4- (VI) or a 5 : 6 : 7-trihydroxybenzanthrone. For reasons given later, the first of these constitutions appears to be preferable.



(V.)



(VI.)



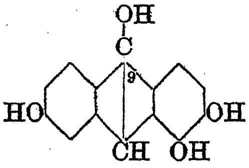
(VII.)

The substance dyes shades distinct from and weaker than those given by anthragallol.

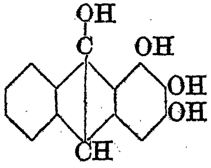
Crude deoxyflavopurpurin from commercial flavopurpurin gives an amorphous acetyl derivative (compare Liebermann, *loc. cit.*; Graebe and Thode, and Bernhard, *Annalen*, 1906, **349**, 207, 222), and cannot be purified in the same way as anthrapurpurin-anthranol (Goodall and Perkin, J., 1924, **125**, 470). A crystalline acetyl compound of the pure substance has also not been described. It is now found that if crude flavopurpurin, crystallised from nitrobenzene, is reduced to the anthranol, and the product is partly acetylated in the cold, a crude *diacetyl* derivative is obtained which can be freed by recrystallisation from the acetyldeoxyanthraflavic acid which is present. The pure diacetyl compound thus obtained is converted by Fischer and Bergmann's method of acetylation (*Ber.*, 1918, **51**, 1797) into *tetra-acetyldeoxyflavopurpurin*, which is readily obtained pure in pale yellow plates. Hydrolysis of this yields deoxyflavopurpurin, which crystallises in deep yellow plates.

iso*Benzflavopurpurin*, $C_{17}H_{10}O_4$, was obtained from flavopurpurin-anthranol by the acraldehyde method. By methylation, only a *dimethyl ether* could be obtained, although the formation from the latter of a *potassium* salt was evidence of the presence of a third hydroxyl group. Acetylation in the ordinary manner gave a *diacetyl* compound, and only by prolonged treatment in boiling solution could a mixture of di- and tri-acetyl derivatives be produced. *iso*Benzflavopurpurin is thus either 2 : 5 : 6- (VII) or 3 : 4 : 7-tri-hydroxybenzanthrone, and of these the former constitution is to be preferred.

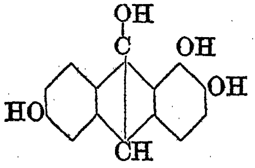
These results therefore indicate that the hydroxyl groups in anthrapurpurin-, anthragallol-, and flavopurpurin-anthranols are present respectively in the 3 : 4 : 6 (VIII), 1 : 2 : 3 (IX), and 1 : 2 : 6 (X) positions.



(VIII.)



(IX.)



(X.)

Miller and Perkin (*loc. cit.*) suggested that the reduction of a hydroxyanthraquinone to its anthranol or anthrone will take place in such a way that any β-hydroxyl in the former will preferably occupy a para-position with respect to the anthranol hydroxyl (9) or anthrone carbonyl group in the latter. Although the conditions dealt with in the present communication differ from those discussed on the former occasion, because two β-hydroxyls are present in all the hydroxyanthraquinones now studied, it will be observed, on examining the formulæ of the hydroxyanthranols given above, that this suggestion still holds good in the case of one β-hydroxyl group at least. The presence of such a hydroxyl in a hydroxyanthraquinone seems, therefore, to be a determining factor in the orientation of the hydroxyls of the anthranol derived from it by reduction. Moreover, it is now suggested as likely that in all cases where the β-hydroxyl is present in the anthranol in the 3- or 6-position, and the contiguous α-position is free, the benzanthrone condensation will take place at the latter point; for instance, 3-hydroxyanthranol gives 2-hydroxybenzanthrone, and anthrapurpurin(3 : 4 : 6-trihydroxy)-anthranol gives 2 : 7 : 8-trihydroxybenzanthrone. It is therefore considered probable that the trihydroxybenzanthrones derived from anthragallol- (IX) and flavopurpurin- (X) anthranols will be represented by the formulæ (VI) and (VII).

Interesting again is the fact that 3-hydroxyanthranol, on treatment with alkali and glucose (Bradshaw and Perkin, J., 1922, **121**, 911), yields 2-hydroxybenzanthronecarboxylic acid.

Benzalizarin (III) and benzanthrapurpurin (IV) are red substances and their dyeing properties resemble those of alizarin and anthrapurpurin, respectively. *iso*Benzflavopurpurin (VII) dyes yellow shades of a similar character to those of *iso*benzalizarin (V) and differs markedly from flavopurpurin in this respect. According to the quinonoid theory, (III) and (IV) can only be represented as *p*-quinonoid and (V) and (VII) as *o*-quinonoid dyes, and, as suggested in a previous communication (*loc. cit.*), the very distinct shades of red and yellow given by these colouring matters respectively are explainable on the assumption that they possess such configurations. On the other hand, *iso*benzanthragallol (VI), as its formula suggests, may be represented as either a *p*- or an *o*-quinonoid dye, though its somewhat feeble tinctorial property favours the latter view.

EXPERIMENTAL.

Benzanthrapurpurin.—A mixture of anthrapurpurin-anthranol (4 g.; prepared by hydrolysis of pure acetylanthrapurpurin-anthranol: Goodall and Perkin, *loc. cit.*), sulphuric acid (47 c.c.), water (23 c.c.), and glycerol (8 g.) was slowly heated to 125—130° with constant stirring and kept at that temperature for 1 hour. The dark red solution, when cold, was poured into water, the precipitate was collected, washed, dried, and repeatedly extracted with boiling alcohol, and the extracts were concentrated and poured into much ether. The solution was filtered, well washed, and evaporated, and the dark brown residue (3·1 g.) was digested with acetic anhydride and a trace of pyridine. The product, after repeated crystallisation from acetic acid (charcoal), was obtained in yellow plates (1·9 g.), m. p. 245—246° (Found: C, 68·3; H, 4·2; $C_2H_4O_2$, 44·7. $C_{23}H_{16}O_7$ requires C, 68·3; H, 4·0; $C_2H_4O_2$, 44·55%).

This compound, evidently *triacetylbenzanthrapurpurin*, gave with sulphuric acid a deep red solution, which gradually deposited crimson, microscopic needles of *benzanthrapurpurin sulphate*. These were collected, washed with glacial acetic acid, and dried at 100° (Found: $C_{17}H_{10}O_4$, 73·75. $C_{17}H_{10}O_4,H_2SO_4$ requires $C_{17}H_{10}O_4$, 73·9%).

The *benzanthrapurpurin* obtained from this salt by the action of boiling water crystallised from dilute alcohol in microscopic, orange needles which did not melt below 340° and dissolved in caustic soda solution with a violet coloration. It produced light brown, orange, dull maroon, and dark brown shades on wool mordanted with aluminium, tin, chromium, and iron respectively.

Methylation. To a boiling mixture of acetylbenzanthrapurpurin (2 g.), methyl alcohol (30 c.c.), and methyl iodide (12 c.c.), a solution of caustic potash (2 g.*) in methyl alcohol was gradually added during 12 hours. The excess of methyl iodide was distilled off, the deep reddish-brown liquid was kept over-night, and the crystals that separated were washed with water and dried. The light brown product (0·98 g.) was dissolved in benzene, and a small amount of alcoholic potash added to precipitate any dimethyl ether present as potassium salt. The filtered and concentrated solution deposited crystals over-night, which, by recrystallisation from benzene (charcoal), were obtained in golden-yellow needles (0·45 g.), m. p. 185—185·5° (Found: C, 74·9; H, 4·9; CH_3, 13·7. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0; CH_3, 14·1%).

This compound, *benzanthrapurpurin trimethyl ether*, could also be obtained by methylating benzanthrapurpurin with methyl sulphate in the usual manner.

To demethylate this compound completely, it was necessary to perform the Zeisel determination twice on the same material, as was the case with benzalizarin dimethyl ether (Perkin, J., 1920, **117**, 696).

iso*Benzanthragallol.*—A mixture of anthragallol-anthranol (2 g.), glycerol (50 g.), and powdered anhydrous potassium hydrogen sulphate (20 g.), made into a smooth paste, was gradually heated, with stirring, to 190—200°; the solution was maintained at this temperature for ½ hour, a light brown powder separating. The mixture was cooled somewhat and poured into water, and the precipitate thus produced was washed by decantation, dried, and extracted two or three times with cold alcohol to remove resinous impurities. The product was acetylated, and the crystals that separated (0·9 g.) were recrystallised repeatedly from acetic acid, giving yellow needles of *diacetyl*iso*benzanthragallol*, m. p. 232—233° (Found: C, 69·5; H, 4·0; $C_2H_4O_2$, 32·75. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·9; $C_2H_4O_2$, 33·15%).

This diacetyl compound, when hydrolysed with hydrochloric and acetic acids, gave 77·06% of iso*benzanthragallol* (calc., 76·8%). The latter crystallised from nitrobenzene in yellow needles, m. p. 319—321° (decomp.), sparingly soluble in alcohol, ether, benzene, or acetic acid (Found: C, 73·3; H, 3·8. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%).

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* Commercial stick. Theory requires 1·66 g. KOH for hydrolysis and methylation.

*iso*Benzanthragallol becomes blood-red, without apparently dissolving, on treatment with caustic soda solution, and dyes mordanted woollen cloth shades which are distinct from those given by anthragallol. Pale brown, yellow, light brown, and olive shades are obtained on aluminium, tin, chromium, and iron mordants, respectively.

By prolonged digestion (27 hours) with acetic anhydride and a trace of pyridine, the diacetyl derivative only could be obtained. Acetylation in the cold by Fischer and Bergmann's method (*loc. cit.*) yielded, at least mainly, the diacetyl derivative, without apparent solution of the *iso*benzanthragallol.

iso*Benzanthragallol Dimethyl Ether.*—As experiment showed that methylation of *iso*benzanthragallol could not be effected with methyl iodide or methyl sulphate in the usual way, a suspension of *iso*benzanthragallol (1·5 g.) in dry ether (120 c.c.) was treated with diazomethane (generated from 6 c.c. of nitrosomethylurethane) and kept over-night. The excess of diazomethane was then removed, the solution filtered from unchanged *iso*benzanthragallol (0·8 g.), the filtrate evaporated to dryness, and the residue washed with a little acetone to remove resinous matter. There was thus obtained a yellow, crystalline powder (0·22 g.), and a further small amount (0·03 g.) was deposited from the acetone washings after concentration. By repeated crystallisation from benzene (animal charcoal), yellow needles of iso*benzanthragallol dimethyl ether*, m. p. 152—153°, were obtained (Found: C, 74·5; H, 4·7; CH_3, 9·8. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6; CH_3, 9·8%). The final acetone filtrate contained much resinous matter from which nothing definite could be isolated.

In the Zeisel determination, it was found necessary to submit the substance to a second distillation with hydriodic acid. The residue, after treatment with bisulphite solution, consisted of *iso*benzanthragallol.

*iso*Benzanthragallol dimethyl ether did not yield an acetyl derivative even by prolonged digestion (5 hours) with acetic anhydride and pyridine. It was soluble with difficulty in absolute alcohol, yielding a faintly yellow solution which, on the addition of alcoholic potash, became of a somewhat deeper colour. On keeping, pale yellow, hair-like, silky needles separated which were washed with alcohol and dried. They darkened at 130°, melted at 235—240°

to form a black liquid, gave ash on ignition, and evidently consisted of the monopotassium salt of *iso*benzanthragallol dimethyl ether. A suspension in absolute alcohol to which a trace of phenolphthalein was added showed no red coloration, but on addition of water this was observed owing to decomposition of the potassium salt.

Methylation. To a boiling suspension of *iso*benzanthragallol dimethyl ether (0·5 g.) in methyl alcohol (10 c.c.) and methyl iodide (3 c.c.), a solution of caustic potash (0·12 g.*) in methyl alcohol was gradually added during 11 hours, and the digestion was continued for 2—3 hours longer. The excess of methyl iodide was removed, and after 12 hours the crystals were collected, washed with methyl alcohol and with water, and dried. The yellow, microscopic needles (0·45 g.), m. p. 152—153°, were shown to consist entirely of unchanged *iso*benzanthragallol dimethyl ether by a mixed m.-p. determination.

Flavopurpurin-anthranol.—Commercial flavopurpurin (10 g.), partly purified by crystallisation from nitrobenzene, was treated for 1 hour with a boiling solution of stannous chloride (10 parts) in hydrochloric acid (50 parts). When cold, the product was collected, washed with hydrochloric acid and with water, and dried. The light brown powder (8·7 g.), on treatment with acetic anhydride and potassium acetate in the cold, slowly dissolved, but after a short time crystals separated; after 12 hours, these were collected and washed with alcohol (yield, 4·3 g.). By repeated crystallisation from acetic acid (charcoal), this *acetyl* derivative was obtained in yellow plates (2·2 g.), m. p. 209—212° (Found: C, 66·2; H, 4·4; $C_2H_4O_2$, 36·6. $C_{18}H_{14}O_6$ requires C, 66·25; H, 4·3; $C_2H_4O_2$, 36·8%).

This substance, *diacetylflavopurpurin-anthranol*, was hydrolysed with hydrochloric acid in acetic acid solution in the usual way. The product, by recrystallisation from dilute alcohol, was obtained in deep yellow, rectangular plates which darkened at 200° and melted at 231—233° when slowly heated. If the m.-p. tube, however, was introduced into a bath at 235°, the substance melted at 243—245° (Found: C, 69·4; H, 4·3. Calc. for $C_{14}H_{10}O_4$: C, 69·4; H, 4·1%). Graebe and Thode (*loc. cit.*) described it as a crystalline powder, m. p. 258°. Flavopurpurin-anthranol dissolves in caustic soda solution with an orange-red colour which in air rapidly develops the purple tint characteristic of the alkaline solution of flavopurpurin.

By acetylating diacetylflavopurpurin-anthranol by Fischer and Bergmann's method (*loc. cit.*), *tetra-acetylflavopurpurin-anthranol* was obtained, which, after repeated crystallisation from methyl alcohol, was isolated in very pale yellow, rectangular plates, m. p. 181—182°, sparingly soluble in methyl alcohol with formation of a blue fluorescent solution (Found: C, 64·2; H, 4·5; $C_2H_4O_2$, 58·3. $C_{22}H_{18}O_8$ requires C, 64·4; H, 4·4; $C_2H_4O_2$, 58·5%).

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* Commercial stick. Theory requires 0·09 g. KOH.

Tetra-acetylflavopurpurin-anthranol, on oxidation with chromic acid in acetic acid solution, gave yellow needles of triacetylflavopurpurin, m. p. 208—211° (Frobenius and Hepp, *Ber.*, 1907, **40**, 1049, give m. p. 202—203°).

iso*Benzflavopurpurin.*—Attempts to prepare this substance by the glycerol–sulphuric acid method were unsuccessful, and the following procedure was therefore adopted. Hydrogen chloride was passed into a mixture of diacetylflavopurpurin-anthranol (1 g.), acraldehyde (3 c.c. of a solution of 1 part of acraldehyde in 5 parts of glacial acetic acid), and glacial acetic acid (10 c.c.), and the mixture was heated to the b. p. during ¼ hour and boiled for ¼ hour. The yellow solution became orange as the boiling point was reached, and brown at the end of the operation. The solution, poured into boiling water (150 c.c.), gave a resinous precipitate. This, which solidified when cold, was ground with water, washed, and digested with boiling acetic anhydride and a trace of pyridine. The crystals (0·4 g.) of *diacetyl*iso*benzflavopurpurin* thus obtained separated from acetic acid (charcoal) in yellow needles (0·23 g.), which sintered at 233° and melted at 236° (Found: C, 69·4; H, 3·9; $C_2H_4O_2$, 33·01. $C_{21}H_{14}O_6$ requires C, 69·6; H, 3·9; $C_2H_4O_2$, 33·15%).

Benzanthrapurpurin, *iso*benzanthragallol, and 2-hydroxybenzanthrone, prepared in about 30% yield from anthrapurpurin- and anthragallol-anthranols and 3-hydroxyanthranol, respectively, by this acraldehyde method, were identified by the melting points of their acetyl derivatives.

Diacetyl*iso*benzflavopurpurin, hydrolysed with hydrochloric acid in presence of acetic acid, gave iso*benzflavopurpurin*, which is soluble in alkaline solutions with a yellow colour. It is sparingly soluble in acetic acid, and crystallises therefrom in long, light brown needles containing one molecule of acetic acid of crystallisation (Found: $C_{17}H_{10}O_4$, 82·1. $C_{17}H_{10}O_4+C_2H_4O_2$ requires $C_{17}H_{10}O_4$, 82·25%). These crystals, although stable at 100°, are converted at 160° with loss of acetic acid into dull yellow needles, m. p. 293—295° (decomp.) (Found: C, 73·2; H, 3·7. $C_{17}H_{10}O_4$ requires C, 73·4; H, 3·6%).

*iso*Benzflavopurpurin dyes shades which are quite distinct from those yielded by flavopurpurin. On wool mordanted with aluminium, tin, chromium, and iron, yellow, pale yellow, yellowish-brown, and brown shades are respectively obtained.

By treatment for 5 hours with boiling acetic anhydride and pyridine, *iso*benzflavopurpurin gave a product which melted at 217—221° and consisted of yellow needles, probably of the triacetyl derivative, mixed with clusters of microscopic needles of the diacetyl compound. Even after further prolonged boiling, some diacetyl derivative still remained.

Methylation. A mixture of diacetyl*iso*benzflavopurpurin (1 g.), methyl alcohol (15 c.c.), and methyl iodide (6 c.c.) was boiled for 16 hours, a solution of caustic potash (0·9 g.*) in methyl alcohol being gradually added. From the clear solution at first obtained, a yellow precipitate of the potassium compound of the methyl ether slowly separated, and this was collected, washed with water, and dried. This compound, which did not melt below 300° and gave an ash on ignition, was ground with dilute hydrochloric acid (1 : 4), the mixture boiled, and the precipitate collected (yield, 0·65 g.). The product, now ash-free, crystallised from alcohol–acetic acid in long, light brown needles, m. p. 199—200° (Found : C, 74·3; H, 4·8; CH_3, 9·7. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6; CH_3, 9·8%).

iso*Benzflavopurpurin dimethyl ether* was completely demethylated only after the finely divided substance had been boiled with hydriodic acid for 12 hours.

A solution of the dimethyl ether in absolute alcohol, on addition of alcoholic potash, gave an immediate crystalline precipitate of the monopotassium salt.

We are much indebted to the British Alizarine Co., Ltd., for the commercial anthra- and flavo-purpurin necessary for this investigation.

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[*Received, March 29th*, 1927.]

CLXXXII.—*Reduction Products of the Hydroxyanthraquinones. Part IX.*

By ALEXANDER MACMASTER and ARTHUR GEORGE PERKIN.

THE aluminium–mercury couple, by means of which 2-mono- and 2 : 6-, 2 : 7-, and 1 : 2-di-hydroxyanthracenes were readily obtained from the corresponding hydroxyanthraquinones or their anthranols, and also anthracene from anthraquinone (Hall and Perkin, J., 1923, **123**, 2029), reduces 1-mono-, 1 : 5-di-, and 1 : 2 : 3- and 1 : 2 : 6-tri-hydroxyanthraquinones, not to the hydroxyanthracenes, but only to the hydroxyanthranols. The stability of these hydroxyanthranols is thus evidently due to the effect of one or other of the hydroxyls present therein, and these it is now known occupy the 1-, 1 : 5-, 1 : 2 : 3-, and 1 : 2 : 6-positions, respectively (Cross and Perkin, preceding paper). There is evidence that in compounds of this type a residual affinity exists between the hydroxyls in positions 1 and 9, as, for instance, in quinizarin, which is reduced by stannous chloride and hydrochloric acid merely to *leuco*-quinizarin (II) and not further to the hydroxyanthranol. The resistance of 1-hydroxyanthranol (I) to reduction by the aluminium–mercury couple also harmonises with this view, but, on the other hand, there are cases where a somewhat similar behaviour is observed with substances of this type in which the 1-hydroxyl is absent. For example, though 3 : 4-dihydroxy(alizarin)-anthranol, on treatment with the couple, readily yields 1 : 2-dihydroxyanthracene, 3 : 4 : 6-trihydroxy(anthrapurpurin)-anthranol gives but traces of a reduction product, which has not yet been isolated pure. As a means of overcoming this difficulty, a preliminary methylation of the hydroxyanthraquinones or their anthranols suggested itself; indeed Ladgozinski (*Annalen*, 1905, **342**, 104) has shown that hystazarin dimethyl ether is readily reduced to 2 : 3-dimethoxyanthracene even with zinc dust and ammonia. There should be, however, no difficulty in preparing 2 : 3-dihydroxyanthracene from hystazarin itself by the aid of the aluminium–mercury couple. The present communication deals with anthrapurpurin trimethyl ether, and this has been converted, by long digestion in alcoholic solution with the couple in presence of ammonia, into 1 : 2 : 7-trimethoxyanthracene in moderate yield. For the preparation of anthrapurpurin trimethyl ether, the method of Graebe and Bernhard (*Annalen*, 1906, **349**, 222) was employed, that is, 3 : 4 : 6-trihydroxyanthranol was methylated and then oxidised with chromic acid. The methylated anthranol, which was not closely examined by those authors, is the 3 : 4 : 6 : 9-tetramethoxy-compound, and this is interesting because the analogous product from deoxyalizarin (3 : 4-dihydroxyanthranol) is 3 : 4-dimethoxyanthrone (Graebe and Thode, *Annalen*, 1906, **349**, 207). In addition to the tetramethoxy-compound, some 3 : 4 : 6-trimethoxyanthranol was produced, a compound which is more readily obtained by the reduction of anthrapurpurin trimethyl

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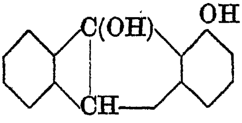
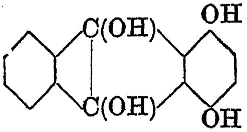
* Commercial stick. Theory requires 0·77 g. KOH for hydrolysis and methylation.

(I.)





(II.)

ether in acetic acid solution with stannous chloride and hydrochloric acid. This with acetic anhydride and pyridine yields the 3 : 4 : 6-trimethoxy-9-acetyl compound. Finally, if air is not excluded during the methylation process, a small amount of 3 : 4 : 6 : 3′ : 4′ : 6′-hexamethoxydianthrone is formed. This can also be prepared by the oxidation of 3 : 4 : 6-trimethoxyanthranol with ferric chloride in presence of acetic acid.

EXPERIMENTAL.

3 : 4 : 6-Trihydroxyanthranol was obtained from commercial anthrapurpurin by reduction with stannous chloride and hydrochloric acid (Goodall and Perkin, J., 1924, **125**, 470), and the acetylated product was crystallised from alcohol–acetic acid until it was free from acetyl*iso*anthraflavic acid anthranol. To a suspension of the product (10 g.) in boiling 80% methyl alcohol (300 c.c.), potassium hydroxide (50 g. in 50 c.c. of water) and methyl sulphate (55 c.c.) were slowly added through capillary tubes attached to the condenser; the mixture was kept slightly alkaline, and access of air was prevented as far as possible. The liquid, after being acidified, slowly deposited crystals, which were washed with dilute alkali solution and dried over sulphuric acid. The pale brown product (yield, 60%) was repeatedly extracted with boiling ligroin (200 c.c.). The extract after concentration deposited pale yellow needles which melted at 107° after recrystallisation (yield, 40%) (Found: C, 72·4; H, 6·0; CH_3, 20·0. $C_{18}H_{18}O_4$ requires C, 72·4; H, 6·0; CH_3, 20·0%). 3 : 4 : 6 : 9-*Tetramethoxyanthranol* gives green, fluorescent solutions, and dissolves in sulphuric acid with a brown colour which changes to purple on addition of a trace of nitric acid. That portion of the methylation product insoluble in ligroin contained, in addition to anthrapurpurin trimethyl ether, a small amount of 3 : 4 : 6-trimethoxyanthrone, a compound described later.

3 : 4 : 6 : 9-Tetramethoxyanthranol (9·5 g.) was oxidised in boiling acetic acid (65 c.c.) with a solution of chromic acid (7 g.) in acetic acid (10 c.c.) and water (15 c.c.). When cold, the anthrapurpurin trimethyl ether was collected and recrystallised from benzene. It melted at 198° (Graebe and Bernhard, *loc. cit.*, give m. p. 201°).

1 : 2 : 7-*Trimethoxyanthracene.*—A solution of anthrapurpurin trimethyl ether (4 g.) in cold sulphuric acid was poured into water, and the precipitate was collected and added in the moist condition to alcohol (100 c.c.). The suspension was boiled and treated with the aluminium–mercury couple (0·5 g.) and concentrated ammonia solution (6 c.c.), these additions being repeated five times during

4 hours. The blue, fluorescent solution, acidified with hydrochloric acid and evaporated to one-fourth of its bulk, deposited crystals (2·2 g.), which were washed with dilute alkali solution and recrystallised from ligroin (yield, 1·8 g.) (Found: C, 75·8; H, 5·9; CH_3, 16·3. $C_{17}H_{16}O_3$ requires C, 75·55; H, 5·9; CH_3, 16·7%). 1 : 2 : 7-*Trimethoxyanthracene* forms prismatic needles which melt at 95° and are very soluble in the usual solvents. Its solutions in benzene and alcohol are fluorescent. The solution in sulphuric acid is orange-yellow, but on gentle heating becomes a plum-coloured liquid with a green fluorescence, a type of colour change common to the hydroxyanthracenes (Hall and Perkin, *loc. cit.*, p. 2032).

3 : 4 : 6-*Trimethoxyanthranol.*—To a boiling solution of stannous chloride (10 g.) in hydrochloric acid (25 c.c.), anthrapurpurin trimethyl ether (1 g.), dissolved in acetic acid (30 c.c.), was added, and the digestion continued for 1 hour. The liquid, diluted with hot hydrochloric acid, deposited canary-yellow crystals, which became almost colourless after washing (yield, 0·9 g.) and were obtained in needles, m. p. 149°, by recrystallisation from alcohol (Found: C, 71·85; H, 5·5; CH_3, 15·4. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6; CH_3, 15·8%). 9-*Acetyl*-3 : 4 : 6-*trimethoxyanthranol*, obtained by acetylation in the usual manner, formed colourless needles, m. p. 127° (Found: $C_2H_4O_2$, 13·9. $C_{19}H_{18}O_5$ requires $C_2H_4O_2$, 13·2%).

3 : 4 : 6 : 3′ : 4′ : 6′-*Hexamethoxydianthrone.*—A solution of 3 : 4 : 6-trimethoxyanthranol (7 g.) in acetic acid (25 c.c.) was treated with commercial ferric chloride (10 g.) in acetic acid (10 c.c.) and gently boiled for 2 hours. When cold, the crystals were collected, washed with alcohol, and recrystallised from alcohol–acetic acid (Found: C, 72·3; H, 5·2; CH_3, 15·6. $C_{34}H_{30}O_8$ requires C, 72·1; H, 5·3; CH_3, 15·9%). The *hexamethoxy*-compound forms colourless needles which are very sparingly soluble in alcohol, melt at 224°, and dissolve in sulphuric acid with a yellow colour which becomes purple on heating. It does not appear to enolise readily and does not pass into the acetyldianthranol when digested with boiling acetic anhydride and pyridine. Attempts to convert this compound into the corresponding dianthraquinone and helianthrone have as yet been unsuccessful.

Our thanks are due to the British Alizarine Co., Ltd., for the commercial anthrapurpurin employed in this investigation.

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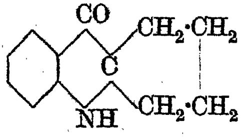
[*Received, March 29th*, 1927.]

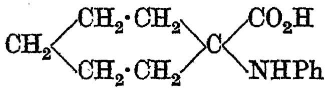
CLXXXIII.—*The Reactions of* 1-*Anilino*cyclo*hexane*-1-*carboxylic Acid. Synthesis of ψ-Indoxyl*spirocyclo*hexane.*

By RAYMOND LIVINGSTON BETTS, RUDOLPH MUSPRATT, and SYDNEY GLENN PRESTON PLANT.

IT was shown by Plant and Facer (J., 1925, **127**, 2037) that the fusion of 1-anilino*cyclo*pentane-1-carboxylic acid with a mixture of potassium hydroxide and sodium ethoxide, under conditions similar to those used by Bucherer and Grolée (*Ber.*, 1906, **39**, 986) for the preparation of 2 : 2-dimethyl-ψ-indoxyl from α-anilino*iso*butyric acid, yielded carbazole and not the expected ψ-indoxyl*spirocyclo*pentane (I). We have now prepared 1-*anilino*cyclo*hexane*-1-*carboxylic acid* (II) by the hydrolysis, first to the *amide*, of 1-anilino-1-cyano*cyclo*hexane, described by Walther and Hübner (*J. pr. Chem.*, 1916, **93**, 124), and we find that this compound differs fundamentally in some of its reactions from the corresponding derivative of *cyclo*pentane. When heated with potassium hydroxide, it gave *ψ-indoxyl*spirocyclo*hexane* (III) in comparatively good yield. ψ-Indoxyl*spirocyclo*pentane has been obtained by a series of reactions from

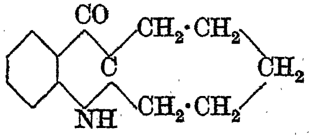
(I.)



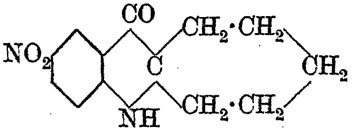


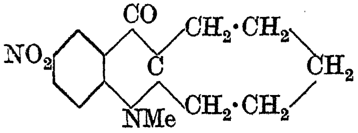
(II.)

(III.)



tetrahydrocarbazole (Perkin and Plant, J., 1923, **123**, 676) and, owing to the fact that it gives a number of interesting derivatives, including co-ordinated compounds of the alkali metals (Sidgwick and Plant, J., 1925, **127**, 209), it was hoped to obtain confirmatory evidence for its structure by synthesis from 1-anilino*cyclo*pentane-1-carboxylic acid by the method mentioned above. Although this led to other results, we now find that the reactions of ψ-indoxyl*spirocyclo*hexane are so similar to those observed with ψ-indoxyl*spirocyclo*pentane that they amply confirm the structure assigned to the latter compound. ψ-Indoxyl*spirocyclo*hexane can be acetylated, and is easily nitrated by dilute nitric acid to give 10-*nitro-ψ-indoxyl*spirocyclo*hexane* (IV), which gives a characteristic sodium derivative, from which 10-*nitro-7-methyl-ψ-indoxyl*spirocyclo*hexane* (V) can readily be obtained. The conditions required for these reactions and the characteristic properties of the


(IV.)


(V.)

products are exactly those observed in the corresponding *cyclo*pentane series. Like ψ-indoxyl*spirocyclo*pentane, ψ-indoxyl*spirocyclo*hexane could not be made to give a nitroso-derivative or a semicarbazone. The behaviour of these two compounds towards sodium hydroxide is fundamentally similar. Only on heating with concentrated aqueous sodium hydroxide is a metallic derivative obtained, and, in both cases, water instantaneously brings about hydrolysis of the product, but whilst the sodium derivative of ψ-indoxyl*spirocyclo*pentane can be obtained with a second molecule of ψ-indoxyl*spirocyclo*pentane attached to it by co-ordinate links, similar conditions gave only the simple sodium salt of ψ-indoxyl*spirocyclo*hexane. There is here no fundamental difference between the two compounds, since the isolation of these co-ordinated compounds in this series must depend upon a number of arbitrary factors, such as the melting point.

It has been shown (Plant and Facer, *loc. cit.*) that 1-anilino*cyclo*pentane-1-carboxylic acid, on heating, loses aniline and water to give the lactone of 1-1′-hydroxy*cyclo*pentane-1′-carboxylylanilino*cyclo*pentane-1-carboxylic acid. 1-Anilino*cyclo*hexane-1-carboxylic acid does not appear to undergo this reaction, but breaks up into aniline and Δ^1-*cyclo*hexene-1-carboxylic acid.

EXPERIMENTAL.

1-*Anilino*cyclo*hexane*-1-*carboxylic Acid* (II).—1-Anilino-1-cyano*cyclo*hexane was prepared by Walther and Hübner's method (*loc. cit.*). The *nitrosoamine* separated when its solution in alcohol containing hydrochloric acid was treated with concentrated aqueous sodium nitrite, and, after recrystallisation from methyl alcohol, it was obtained in pale yellow prisms, m. p. 70°. When a solution of 1-anilino-1-cyano*cyclo*hexane in concentrated sulphuric acid was kept for 2 days at room temperature and then poured on ice, and the mixture was made alkaline with ammonia, 1-*anilino*cyclo*hexane*-1-*carboxylamide* separated quantitatively in a pure condition. It crystallised from dilute alcohol in colourless plates, m. p. 148°

(Found: N, 12·4. $C_{13}H_{18}ON_2$ requires N, 12·8%). The *nitrosoamine* separated from methyl alcohol in pale yellow prisms, m. p. 172°. This amide was comparatively stable and hydrolysis to the corresponding acid was complete only after prolonged boiling with hydrochloric acid. On rubbing with concentrated hydrochloric acid, the *hydrochloride* of the amide separated; a paste of this was added to an excess of hydrochloric acid, and the mixture was boiled under reflux with continuous stirring for 12 hours and then evaporated to dryness. The residue was heated with an excess of dilute aqueous sodium hydroxide, and the solution was filtered and acidified with glacial acetic acid; 1-*anilino*cyclo*hexane*-1-*carboxylic acid* then separated. After recrystallisation from alcohol, it was obtained in colourless prisms, m. p. 142° (Found: N, 6·2. $C_{13}H_{17}O_2N$ requires N, 6·3%).

1-Anilino*cyclo*hexane-1-carboxylic acid was heated in a distillation flask, and the oily distillate treated with an excess of dilute hydrochloric acid; the undissolved portion then soon solidified. This product melted at 29—31° and was identified as Δ^1-*cyclo*hexene-1-carboxylic acid (compare Aschan, *Annalen*, 1892, **271**, 267). It was readily soluble in dilute aqueous sodium carbonate, from which it was reprecipitated by the addition of hydrochloric acid. Its solution in chloroform, after addition of the calculated amount of bromine, was kept for 2 hours, the solvent removed by evaporation, and the residue recrystallised from benzene–petroleum, from which 1 : 2-dibromo*cyclo*hexane-1-carboxylic acid separated in colourless prisms, m. p. 144° (compare Aschan, *loc. cit.*). That portion of the distillate which dissolved in dilute hydrochloric acid was identified as aniline by conversion into acetanilide.

*ψ-Indoxyl*spirocyclo*hexane* (III).—A mixture of 1-anilino*cyclo*hexane-1-carboxylic acid (35 g.) and potassium hydroxide (90 g.) was heated to 340—350°, maintained at that temperature for ½ hour, allowed to cool, and treated with an excess of water. The insoluble portion was ground with water and dried in a desiccator over sulphuric acid. The crude product (14 g., melting indefinitely at about 80°) was distilled; the yellow, oily distillate solidified on rubbing with petroleum. After recrystallisation from petroleum, the product (m. p. 110—117°) was further purified by boiling it with acetic anhydride (50 c.c.) for an hour, cooling the solution and shaking it with an excess of water, and recrystallising the 7-*acetyl*-*ψ-indoxyl*spirocyclo*hexane* so obtained from methyl alcohol, from which it separated in large, colourless prisms (6 g.), m. p. 105° (Found: N, 5·7. $C_{15}H_{17}O_2N$ requires N, 5·7%). A solution of the acetyl derivative in alcohol (90 c.c.) and water (60 c.c.), containing potassium hydroxide (18 g.), was boiled for ½ hour and thereafter diluted with water; *ψ-indoxyl*spirocyclo*hexane* (4 g.) then separated in a pure condition. It can be crystallised from petroleum and obtained in colourless prisms, m. p. 124° (Found: C, 77·8; H, 7·5; N, 6·8. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·4; N, 7·0%).

ψ-Indoxyl*spirocyclo*hexane is not altered, even on boiling, by dilute hydrochloric acid or dilute sodium hydroxide solution. When heated in a steel tube at 200—210° with an excess of 20% aqueous sodium hydroxide, it was converted into a *sodium* derivative, which could be removed by filtration through asbestos. The sodium derivative (Found: Na, 9·7. $C_{13}H_{14}ONNa$ requires Na, 10·3%) did not melt up to 350° and was immediately hydrolysed, on grinding with water, to give ψ-indoxyl*spirocyclo*hexane. On warming with dry benzene or toluene, the substance dissolved almost completely, and on filtering and cooling the solution ψ-indoxyl*spirocyclo*hexane separated—which seems to indicate that combined water is present in the sodium derivative.

When a solution of ψ-indoxyl*spirocyclo*hexane in alcohol was treated with a few drops of concentrated hydrochloric acid and a few drops of a concentrated solution of sodium nitrite, kept for 15 minutes, and then diluted with water, the substance was recovered completely unchanged. The substance was also recovered unchanged from attempts to make a semicarbazone.

When ψ-indoxyl*spirocyclo*hexane (3 g.) was heated with a mixture of nitric acid (30 c.c. of *d* 1·4) and water (120 c.c.), the liquid at first became green and a dark green oil separated. The colour rapidly changed to yellow and, after boiling for 3 minutes, the mixture was cooled and the solid recrystallised from dilute alcohol, from which 10-*nitro-ψ-indoxyl*spirocyclo*hexane* separated in pink prisms, m. p. 177—178° (Found: N, 11·3. $C_{13}H_{14}O_3N_2$ requires N, 11·4%). 10-Nitro-ψ-indoxyl*spirocyclo*hexane is soluble in very dilute aqueous sodium hydroxide to give a deep yellow solution, but from more concentrated solutions the sodium salt separates as a yellow solid, which may be dissolved by warming. When an excess of methyl sulphate was shaken with the warm solution in aqueous sodium hydroxide, a yellow product immediately separated, and, after recrystallisation from dilute alcohol, 10-*nitro*-7-*methyl-ψ-indoxyl*spirocyclo*hexane* was obtained in yellow plates, m. p. 129° (Found: N, 10·9. $C_{14}H_{16}O_3N_2$ requires N, 10·8%). No methyl iodide was obtained on heating the substance with hydriodic acid under the usual conditions of a Zeisel experiment, so it is evident that the methyl group is attached to nitrogen and is not present as methoxyl.

One of the authors (R. L. B.) wishes to thank the Imperial Order of the Daughters of the Empire (Canada) for a scholarship which enabled him to take part in the research.

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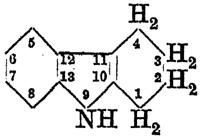
[*Received, April 8th*, 1927.]

CLXXXIV.—*Substitution in Hexahydrocarbazole Derivatives.*

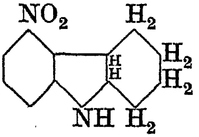
By JOHN GURNEY and SYDNEY GLENN PRESTON PLANT.

THE action of nitric acid on tetrahydrocarbazole (I) and its 9-acyl derivatives was found to give rise, among other products, to nitro-compounds which appeared at first sight to be formed by a reversal of the ordinary rules of substitution (Perkin and Plant, J., 1921, **119**, 1825; 1923, **123**, 676). The double linking in tetrahydrocarbazole has been shown to be a very active one, and the formation of these compounds can be explained, as was pointed out by Professor Robinson, by taking the view that the orienting influence is transmitted through this linking. In hexahydrocarbazole, this double bond is absent, and the introduction of substituents into this molecule ought to give results which are different from those observed with tetrahydrocarbazole. We have now investigated this problem and established the constitutions of the products with respect to those of the corresponding tetrahydrocarbazole derivatives.

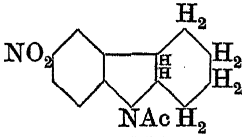
The structures assigned to the nitro-compounds obtained from hexahydrocarbazole and its 9-acyl derivatives depend upon the configurations of the four isomeric mononitrotetrahydrocarbazoles. Three of these are obtained synthetically from *cyclo*hexanone-*o*-, -*m*-, and -*p*-nitrophenylhydrazone, respectively, by Fischer's indole synthesis (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 53), whilst the fourth is prepared from 9-acetyltetrahydrocarbazole (Perkin and Plant, *loc. cit.*). There is no doubt at all about the configurations of 6-nitro- and 8-nitro-tetrahydrocarbazole. The sole product obtained when ring closure takes place by loss of ammonia from *cyclo*hexanone-*m*-nitrophenylhydrazone has been assumed by Borsche, Witte, and Bothe to be 7-nitrotetrahydrocarbazole, but it may possibly be the 5-nitro-compound, whilst the fourth isomeride, assumed in consequence by Perkin and Plant to be 5-nitrotetrahydrocarbazole, may be the 7-nitro-derivative. Ring closure in the case of the corresponding *cyclo*hexanone-*m*-carboxyphenylhydrazone does, in fact, give both of the two alternative products (Collar and Plant, J., 1926, 808). Both the 5- and the 7-position are, however, meta with respect to the >NH group.



(I.)



(II.)



(III.)

The nitration of hexahydrocarbazole in concentrated sulphuric acid solution gives a single product, which has been identified as 5-*nitrohexahydrocarbazole* (II). Its structure has been established by reducing it to the corresponding 5-*aminohexahydrocarbazole*, which has also been prepared by the reduction of 5-aminotetrahydrocarbazole. The nitration of 9-methylhexahydrocarbazole under the same conditions gives a product which must be 5-*nitro*-9-*methylhexahydrocarbazole*, since it is identical with the substance obtained by methylating 5-nitrohexahydrocarbazole. Von Braun and Ritter (*Ber.*, 1922, **55**, 3802) nitrated 9-ethylhexahydrocarbazole in concentrated sulphuric acid and obtained a compound, m. p. 142°, which they assumed, without proof, to be 7-nitro-9-ethylhexahydrocarbazole. If the structures assigned to the nitrotetrahydrocarbazoles are correct, this substance is 5-nitro-9-ethylhexahydrocarbazole, since it can also be obtained by ethylation of 5-nitrohexahydrocarbazole. In any case, the statement of von Braun and Ritter that the nitro-group takes up a position which is meta with respect to the >NH group is correct.

The action of nitric acid on 9-acetylhexahydrocarbazole in glacial acetic acid gave unexpected products. From the reaction mixture, 6-*nitro*-9-*acetylhexahydrocarbazole* (III) was isolated. The structure of this compound was established by hydrolysing it to 6-*nitrohexahydrocarbazole* and reducing the latter to the corresponding *amine*, which gave a *diacetyl* derivative on treatment with acetic anhydride. The same diacetyl derivative was obtained when 6-aminotetrahydrocarbazole was reduced electrolytically, and the product treated in the same way with acetic anhydride. In addition to 6-nitro-9-acetylhexahydrocarbazole, 5-nitro-9-acetyltetrahydrocarbazole and 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole were isolated in considerable quantities from the product. The latter two substances are the compounds formed when nitric acid acts under the same conditions on 9-acetyltetrahydrocarbazole (Perkin and Plant, *loc. cit.*). It thus appears that only a portion of the 9-acetylhexahydrocarbazole undergoes nitration under these conditions, the remainder being oxidised to 9-acetyltetrahydrocarbazole, which is then acted on by more nitric acid in the way previously established. In concentrated sulphuric acid, nitration of 9-acetylhexahydrocarbazole to the 6-nitro-derivative proceeds without any appreciable side reactions.

When nitric acid was allowed to react with 9-benzoylhexahydrocarbazole in glacial acetic acid, some oxidation to 9-benzoyltetrahydrocarbazole again first took place. The isolation of all the products of this reaction in a pure state was not achieved on account of their great solubility in acetic acid, but on using a small quantity of solvent and seeding the solution with a crystal of 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole, there separated a considerable quantity of that substance, which is one of the two products obtained when nitric acid acts on 9-benzoyltetrahydrocarbazole (Perkin and Plant, *loc. cit.*; 9-benzoyltetrahydrocarbazole and 9-acetyltetrahydrocarbazole react in different ways with nitric acid). Direct nitration of 9-benzoylhexahydrocarbazole was accomplished in concentrated sulphuric acid, the product being 6-*nitro*-9-*benzoylhexahydrocarbazole*, its structure being established by the fact that it gave 6-nitrohexahydrocarbazole, identical with the substance obtained from 9-acetylhexahydrocarbazole, on hydrolysis.

Bromination of hexahydrocarbazole in glacial acetic acid gave 6-*bromohexahydrocarbazole*, the structure of which is established by the fact that it is identical with 6-bromohexahydrocarbazole prepared by the reduction of 6-bromotetrahydrocarbazole. The bromination of 9-acetyl- and 9-benzoyl-hexahydrocarbazole proceeded in the same way to give 6-*bromo*-9-*acetylhexahydrocarbazole* and 6-*bromo*-9-*benzoylhexahydrocarbazole* respectively, both of which gave 6-bromohexahydrocarbazole on hydrolysis.

It is clear from these results that substitution in hexahydrocarbazole takes quite a different course from that observed with tetrahydrocarbazole, and that the compound may be considered for this purpose as a simple benzene derivative.

EXPERIMENTAL.

The Nitration of Hexahydrocarbazole and 9-*Methylhexahydrocarbazole.*

The hexahydrocarbazole used in these experiments was prepared by the electrolytic reduction of tetrahydrocarbazole (see Perkin and Plant, J., 1924, **125**, 1512).

5-*Nitrohexahydrocarbazole.*—A solution of hexahydrocarbazole (30 g.) in concentrated sulphuric acid (300 c.c.) was treated gradually with powdered potassium nitrate (17·5 g.), the temperature being kept at 3°, allowed to remain for 15 minutes, and then poured on ice. The solution was kept at 0° by the addition of ice, and made alkaline with ammonia; the oily product then soon solidified (m. p. 68°).

After crystallisation from alcohol, *5-nitrohexahydrocarbazole* was obtained in lemon-yellow needles, m. p. 69° (Found: N, 12·8. $C_{12}H_{14}O_2N_2$ requires N, 12·8%). *5-Nitro-9-acetylhexahydrocarbazole* was obtained when a mixture of 5-nitrohexahydrocarbazole (5 g.) and acetic anhydride (10 g.) was kept at 110° for 3 hours, cooled, and shaken with an excess of water. It separated from alcohol in pale yellow, square plates, m. p. 142° (Found: N, 10·5. $C_{14}H_{16}O_3N_2$ requires N, 10·8%).

5-Aminohexahydrocarbazole.—A solution of 5-nitrohexahydrocarbazole (10 g.) in sulphuric acid (150 c.c. of 60%) was reduced for 10 hours in the cathode compartment of an electrolytic cell, lead electrodes and a current of 4·1 amps. (0·02 amp. per sq. cm. of cathode) being used, and the cell being kept in cold water. After dilution with an equal volume of water and filtering, the mixture was made alkaline with ammonia, crushed ice also being added. The solid product was crystallised from alcohol, from which *5-aminohexahydrocarbazole* separated in colourless prisms, m. p. 111° (Found: N, 14·9. $C_{12}H_{16}N_2$ requires N, 14·9%). Yield, 55% of the theoretical.

5-Aminohexahydrocarbazole was also obtained by reducing a solution of 5-aminotetrahydrocarbazole hydrochloride (3 g., prepared as described by Edwards and Plant, J., 1923, **123**, 2395) in sulphuric acid (100 c.c. of 60%) in the electrolytic cell as before, but keeping it immersed in boiling water for 16 hours. The solution was then filtered and made alkaline at 0° with ammonia, and the product was extracted with ether. After the extract had been dried over potassium carbonate and the solvent removed, the residue solidified on rubbing, and, after recrystallisation from alcohol, 5-aminohexahydrocarbazole (0·4 g.) was obtained in colourless prisms; these, alone or mixed with the 5-aminohexahydrocarbazole described above, melted at 111°.

Both products gave the same diacetyl derivative on being heated with an excess of acetic anhydride at 100° for 15 minutes. After the solution had been cooled, and shaken with an excess of water, the solid obtained was crystallised from acetone, *5-acetamido-9-acetylhexahydrocarbazole* separating in colourless prisms, m. p. 163° (Found: N, 10·1. $C_{16}H_{20}O_2N_2$ requires N, 10·3%).

5-Nitro-9-methylhexahydrocarbazole.—9-Methylhexahydrocarbazole was prepared by the reduction of 9-methyltetrahydrocarbazole (Perkin and Plant, *loc. cit.*). This substance shows a marked tendency to remain in a supercooled condition (a specimen is still completely liquid after 3 years) and has hitherto been described as a colourless oil (see also von Braun and Ritter, *loc. cit.*), but it can be crystallised from alcohol, from which it separates in colourless prisms,

m. p. 50° (Found: N, 7·4. Calc.: N, 7·5%). A solution of 9-methylhexahydrocarbazole (1 g.) in concentrated sulphuric acid (30 c.c.) was treated below 3° with potassium nitrate (0·55 g.), allowed to remain for 5 minutes, poured on ice, made alkaline with ammonia, and saturated with sodium chloride. The solid produced (m. p. 49—50°) was crystallised from alcohol, from which 5-*nitro*-9-*methylhexahydrocarbazole* (0·6 g.) separated in bright yellow needles, m. p. 52° (Found: N, 12·2. $C_{13}H_{16}O_2N_2$ requires N, 12·1%).

5-Nitro-9-methylhexahydrocarbazole was also prepared by heating 5-nitrohexahydrocarbazole (1 g.) with methyl iodide (3·5 g.) in a sealed tube at 100° for 2 hours, removing the excess of methyl iodide, treating the residue with dilute aqueous sodium hydroxide and extracting the solution with ether. After the ether had been removed, the residue was recrystallised from alcohol, from which the product separated in yellow needles; these, alone or mixed with the 5-nitro-9-methylhexahydrocarbazole described above, melted at 50°.

5-*Nitro*-9-*ethylhexahydrocarbazole*.—5-Nitrohexahydrocarbazole was ethylated by a process similar to that described for the methylation, but the reaction was much slower and heating was continued for 18 hours. The product was recrystallised from alcohol, from which 5-nitro-9-ethylhexahydrocarbazole separated in bright yellow prisms, m. p. 143° (Found: N, 11·5. Calc.: N, 11·4%). This product is evidently identical with that described by von Braun and Ritter (*loc. cit.*).

Action of Nitric Acid on 9-*Acetylhexahydrocarbazole.*

A solution of 9-acetylhexahydrocarbazole (50 g., prepared by the direct acetylation of hexahydrocarbazole; Graebe and Adlerskron, *Annalen*, 1880, **202**, 25) in glacial acetic acid (50 c.c.) was treated gradually at 23—25° with a mixture of nitric acid (26·5 g. of *d* 1·4) and glacial acetic acid (75 c.c.). After 2 hours, the mixture was poured into water; the product then gradually solidified to a yellow mass, from which three substances were isolated in a pure condition. After repeated crystallisation from acetone, a small quantity (0·2 g.) of glistening, colourless plates, m. p. 204°, was obtained. An analysis (Found: N, 6·0. Calc.: N, 5·7%) and a mixed m.-p. determination showed that this substance was 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole, one of the products obtained when nitric acid acts on 9-acetyltetrahydrocarbazole in glacial acetic acid. The mixture in the acetone mother-liquor, on repeated crystallisation from glacial acetic acid, yielded yellow needles (5 g.), m. p. 175°, which an analysis (Found: N, 10·8. Calc.: N, 10·9%) and a mixed m.-p. determination proved to be 5-nitro-9-acetyltetrahydrocarbazole, the other of the two products from 9-acetyltetrahydrocarbazole. Further proof of the structure of this compound was obtained on boiling it for a short time with aqueous-alcoholic sodium hydroxide, diluting the solution with water, and recrystallising the product from alcohol, from which 5-nitrotetrahydrocarbazole separated in yellow prisms, m. p. 172°. From the acetone and glacial acetic acid mother-liquors there was isolated by repeated fractional crystallisation a product which ultimately separated from acetone in lemon-yellow prisms (5 g.), m. p. 150°, and was shown to be 6-*nitro*-9-*acetylhexahydrocarbazole* (Found : N, 10·7. $C_{14}H_{16}O_3N_2$ requires N, 10·8%). The solution of this product (1 g.) in a mixture of alcohol (15 c.c.) and aqueous sodium hydroxide (15 c.c. of 30%) was boiled for 20 minutes and then poured into water. After crystallisation from alcohol, 6-*nitrohexahydrocarbazole* was obtained in bright yellow prisms, m. p. 84° (Found : N, 12·6. $C_{12}H_{14}O_2N_2$ requires N, 12·8%).

6-Nitro-9-acetylhexahydrocarbazole is more easily obtained by nitration in concentrated sulphuric acid solution. 9-Acetylhexahydrocarbazole (5 g.), dissolved in sulphuric acid (40 c.c.), was treated with potassium nitrate (2·3 g.) at 5—7°, the solution poured, after a short time, on ice, and the product crystallised from acetone, from which 6-nitro-9-acetylhexahydrocarbazole separated in yellow prisms, m. p. 150°. The m. p. of the mixture with the 6-nitro-9-acetylhexahydrocarbazole described above showed no depression. The hydrolysis of this product was also carried out by heating it for an hour on the steam-bath with concentrated hydrochloric acid, and, on cooling, the *hydrochloride* of 6-nitrohexahydrocarbazole separated. After recrystallisation from alcohol, it was obtained in pale yellow plates, m. p. 199° (Found : N, 11·2. $C_{12}H_{15}O_2N_2Cl$ requires N, 11·0%). This hydrochloride readily yielded 6-nitrohexahydrocarbazole, m. p. 84°, on treatment with dilute aqueous sodium hydroxide.

6-*Aminohexahydrocarbazole*.—A solution of 6-nitrohexahydrocarbazole (5 g.) in sulphuric acid (140 c.c. of 60%) was reduced electrolytically for 15 hours by the method described above, the cell being kept immersed in cold water. After the solution had been diluted with an equal volume of water, filtered, and made alkaline at 0° with concentrated ammonia, the mixture was extracted with ether, and the ethereal solution dried over potassium carbonate. The viscous, oily 6-*aminohexahydrocarbazole* remaining after removal of the ether could not readily be made to crystallise, so it was treated with an excess of acetic anhydride at room temperature. The product separated on rubbing, and, after the whole had been shaken with an excess of water and then crystallised from alcohol, 6-*acetamido*-9-*acetylhexahydrocarbazole* was obtained in colourless needles (1·2 g.), m. p. 213° (Found: N, 10·3. $C_{16}H_{20}O_2N_2$ requires N, 10·3%).

6-Aminohexahydrocarbazole was also obtained by the electrolytic reduction of a solution of 6-aminotetrahydrocarbazole (4 g., prepared as described by Edwards and Plant, *loc. cit.*) in sulphuric acid (120 c.c. of 60%), a current of 5 amps. being used for 22 hours at room temperature. After the solution had been diluted with water (60 c.c.), filtered, and made alkaline with concentrated ammonia at 0°, a colourless solid separated. This (0·5 g.), after crystallisation from toluene, proved to be unchanged 6-aminotetrahydrocarbazole. The aqueous solution was extracted with ether, and from the ethereal solution the oily 6-aminohexahydrocarbazole was obtained as before. On treatment with acetic anhydride as described above, 6-acetamido-9-acetylhexahydrocarbazole (0·5 g.), m. p. 212°, was formed. A mixture of the two products, prepared by different methods, also melted at 212°.

7-*Acetamido*-9-*acetylhexahydrocarbazole*.—This derivative was prepared during the course of the present work, although it has not been required in order to establish the structure of any compound obtained directly from hexahydrocarbazole. A solution of 7-aminotetrahydrocarbazole hydrochloride (4 g., prepared as described by Edwards and Plant, *loc. cit.*) in sulphuric acid (140 c.c. of 60%) was reduced electrolytically by a current of 5 amps. for 36 hours at 100°; it was then diluted with water, made alkaline with ammonia, and shaken with ether. After being dried with potassium carbonate, the ether was removed and 7-*aminohexahydrocarbazole* remained as a brown oil; this was warmed with an excess of acetic anhydride at 100° for a minute and shaken with an excess of water, and the product was crystallised from alcohol, 7-*acetamido*-9-*acetylhexahydrocarbazole* being obtained in colourless prisms, m. p. 233° (Found: N, 10·4. $C_{16}H_{20}O_2N_2$ requires N, 10·3%).

Action of Nitric Acid on 9-Benzoylhexahydrocarbazole.

9-Benzoylhexahydrocarbazole was prepared by shaking a suspension of hexahydrocarbazole in an excess of a 10% aqueous solution of potassium hydroxide with benzoyl chloride (1¼ mols.). The product separated from alcohol in colourless needles, m. p. 106° (compare von Braun, *Ber.*, 1910, **43**, 2880, who describes it as an oil, b. p. 270°/10 mm.) (Found: N, 4·9. Calc.: N, 5·1%). A solution of 9-benzoylhexahydrocarbazole (5 g.) in glacial acetic acid (15 c.c.) was treated at 60—67° with a mixture of nitric acid (1·9 g. of *d* 1·4) and glacial acetic acid (1 c.c.). The product was cooled, a crystal of 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole (prepared from 9-benzoyltetrahydrocarbazole) added, and the whole stirred for 3 hours. The colourless prisms (0·1 g.), m. p. 146°, that separated were shown by a mixed m.-p. determination to be 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole. When the acetic acid mother-liquor was poured into water, a thick, pale yellow oil separated, but attempts to obtain crystalline substances from this were unsuccessful.

6-*Nitro*-9-*benzoylhexahydrocarbazole*.—A solution of 9-benzoylhexahydrocarbazole (25 g.) in concentrated sulphuric acid (200 c.c., was treated gradually at 10—12° with potassium nitrate (9·1 g.), kept for 30 minutes, and then poured on ice. The yellow solid which separated was recrystallised from alcohol, from which 6-*nitro*-9-*benzoylhexahydrocarbazole* separated slowly in clusters of yellow prisms, m. p. 106—107° (Found: N, 8·7. $C_{19}H_{18}O_3N_2$ requires N, 8·7%). When a solution of this nitro-compound (6 g.) in a mixture of alcohol (100 c.c.) and aqueous sodium hydroxide (75 c.c. of 30%) was boiled for 20 minutes and then poured into cold water, 6-nitrohexahydrocarbazole, which separated from alcohol in yellow prisms, m. p. 84°, was precipitated. The m. p. of a mixture of this product and 6-nitrohexahydrocarbazole obtained from the corresponding acetyl derivative showed no depression.

Bromination of Hexahydrocarbazole Derivatives.

6-*Bromohexahydrocarbazole*.—A solution of hexahydrocarbazole (5 g.) in glacial acetic acid (50 c.c.) was treated gradually at room temperature with bromine (1·8 c.c.). An oily product separated, and, after the addition of all the bromine, the mixture was heated for a minute on the steam-bath; a clear solution was then obtained. On cooling, colourless crystals of the *hydrobromide* (6·3 g.), m. p. 203° (decomp.), separated, and this product, when treated with dilute aqueous sodium hydroxide, yielded 6-*bromohexahydrocarbazole*, which separated from alcohol in colourless, pentagonal plates, m. p. 75° (Found: N, 5·8. $C_{12}H_{14}NBr$ requires N, 5·6%).

The preparation of 6-bromohexahydrocarbazole by the electrolytic reduction of 6-bromotetrahydrocarbazole (prepared as described by Borsche, Witte, and Bothe, *loc. cit.*) had previously been carried out by Miss E. I. Postgate. A suspension of 6-bromotetrahydrocarbazole (4 g.) in sulphuric acid (100 c.c. of 60%) was reduced by a current of 5 amps. (0·02 amp. per sq. cm. of cathode) during 7 hours, the cell being immersed in boiling water. After being diluted to 200 c.c. and filtered from any unchanged 6-bromotetrahydrocarbazole, the solution was made alkaline at 0° with concentrated ammonia; the 6-bromohexahydrocarbazole which separated was crystallised from alcohol and obtained in colourless, pentagonal plates, m. p. 75°. The mixture of these two specimens of 6-bromohexahydrocarbazole also melted at 75°.

6-*Bromo*-9-*acetylhexahydrocarbazole*.—A solution of 9-acetylhexahydrocarbazole (15 g.) in glacial acetic acid (24 c.c.) was treated gradually with bromine (3·6 c.c.), the mixture being kept cool in ice-water. When the reaction had finished, the yellow oil which had separated was dissolved by warming the mixture to 60°, and, on cooling and rubbing, a bright yellow, crystalline product, m. p. 132—134° (decomp.), was obtained. This appeared to be a *hydrobromide* of 6-bromo-9-acetylhexahydrocarbazole, since, on warming it with water or, more readily, by treating it with dilute aqueous potassium hydroxide and then recrystallising the product from alcohol, 6-*bromo*-9-*acetylhexahydrocarbazole* was obtained in long, colourless prisms, m. p. 104° (Found: N, 4·8. $C_{14}H_{16}ONBr$ requires N, 4·8%). After a solution of 6-bromo-9-acetylhexahydrocarbazole in aqueous-alcoholic sodium hydroxide had been boiled for 8 hours, it was poured into water, and the product recrystallised from alcohol; 6-bromohexahydrocarbazole, identical in every way with the specimens described above, separated.

6-*Bromo*-9-*benzoylhexahydrocarbazole*.—A solution of 9-benzoylhexahydrocarbazole (5 g.) in glacial acetic acid (20 c.c.) was treated gradually at room temperature with bromine (1 c.c.), then warmed to 60°, diluted with water, and made alkaline with ammonia. The oily product solidified on standing, and, after crystallisation from alcohol, 6-*bromo*-9-*benzoylhexahydrocarbazole* was obtained in colourless needles (4·2 g.), m. p. 125° (Found: N, 3·8. $C_{19}H_{18}ONBr$ requires N, 3·9%). This product was hydrolysed by boiling it with aqueous-alcoholic potassium hydroxide for 10 hours; the mixture was poured into water, and on recrystallising the precipitate from alcohol, 6-bromohexahydrocarbazole, identical with the specimens described above, was obtained.

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[*Received, April 14th*, 1927.]

CLXXXV.—*The Action of Halogen-substituted Phenylhydrazines upon Dihydroxytartaric Acid.*

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The action of hydrazines upon dihydroxytartaric acid was first studied by Ziegler and Locher (*Ber.*, 1887, **20**, 834), but many of their conclusions were later shown to be incorrect. Repetition of their work by Knorr (*Ber.*, 1888, **21**, 1201), Anschutz (*Annalen*, 1896, **294**, 219), and Gnehm and Benda (*Annalen*, 1897, **299**, 100) showed that the nature of the product depends upon the substituents in the nucleus; thus ordinary phenylhydrazine gives the expected osazone, while phenylhydrazine-*p*-sulphonic acid gives a pyrazolone derivative (tartrazine). The unsubstituted osazone may be converted into a pyrazolone derivative corresponding to tartrazine by crystallisation from acetic acid. Gnehm and Benda (*loc. cit.*) made the further important observation that, when this osazone is crystallised from acetic anhydride, water is lost in a second manner giving an acid anhydride isomeric with the pyrazolone derivative.

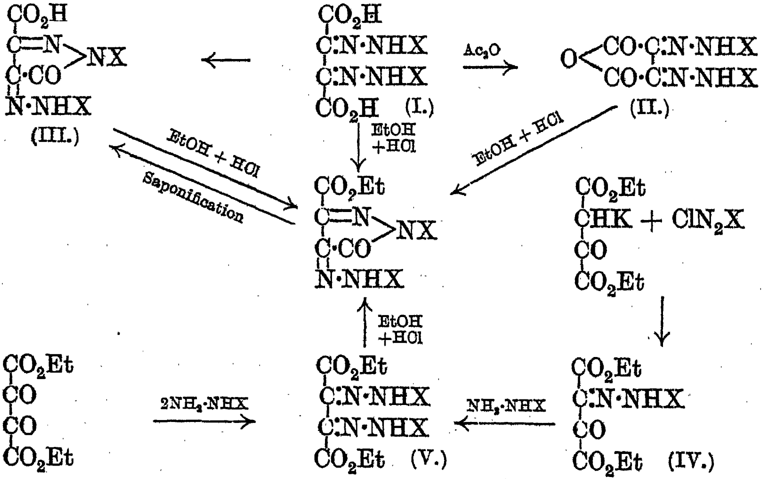
In the present paper, the influence of halogen substituents in the phenyl residues upon the ease of formation from the osazones of the pyrazolone and anhydride ring systems is described. The compounds thus obtained are similar in properties to the corresponding unsubstituted compounds, the accumulation of halogen in the phenyl groups being attended only by a diminishing solubility and a greater tendency towards formation of the anhydride in preference to the pyrazolone.

The osazones are sparingly soluble substances which cannot be crystallised unchanged from any solvent. On heating with acetic anhydride or benzoyl chloride, they are converted into deep red anhydrides. These anhydrides are unaffected by prolonged boiling with water, but dissolve in warm aqueous sodium carbonate to give solutions of the disodium salts of the osazones. On heating with alcohols containing hydrogen chloride, esters of the isomeric pyrazolone acids are formed.

The osazones are converted into hydrazones of diketopyrazolinecarboxylic acids by crystallisation from acetic acid or by acidification of their sodium salts. In the former reaction, varying amounts of the isomeric anhydrides are simultaneously produced. These pyrazoline derivatives are sparingly soluble, yellow or orange-yellow solids which undergo esterification only with difficulty. Their esters are more easily obtained from the corresponding osazone or anhydride.

The structure of the pyrazolone derived from the 2 : 4-dibromophenylosazone has been confirmed by two syntheses.

The following scheme represents the reactions with 2 : 4-dibromophenylhydrazine, X denoting $C_6H_3Br_2$:



EXPERIMENTAL.

Preparation of Sodium Dihydroxytartrate.—Finely powdered tartaric acid (200 g.) is suspended in 280 c.c. of nitric acid (*d* 1·42) and 500 c.c. of concentrated sulphuric acid are added slowly with constant stirring. The temperature rises to about 70° and a clear solution is obtained which is covered over and allowed to cool slowly for 8—12 hours. The semi-solid pulp of tartaric acid dinitrate thus obtained is broken up, and freed from acid as completely as possible by suction and pressure; during this operation the mass should be protected from atmospheric moisture. The hard-pressed, solid mass is stirred with crushed ice until it dissolves, ice-water being added if necessary. The liquid is nearly neutralised with sodium carbonate and, after addition of a litre of saturated sodium acetate solution, filtered and left in a cool place for 2—3 days; at first colourless, it becomes green, owing to the liberation of oxides of nitrogen, and finally colourless when these have escaped. Sodium dihydroxytartrate separates as a very sparingly soluble, white powder, which is filtered off, washed with cold water, and dried by exposure to air.

Preparation of Halogen-substituted Phenylhydrazines.—The reduction of the diazonium salts with stannous chloride, the method previously described for the preparation of the mono- and di-halogen-substituted phenylhydrazines, is not altogether satisfactory on a large scale on account of the cost of the materials and the difficulty of completely removing the tin from the products. The following modification of Fischer's method of reduction with sodium sulphite gives much better results.

A suspension of the finely powdered amine ($\frac{1}{5}$ g.-mol.) in 70 c.c. of concentrated hydrochloric acid (excess) is warmed to about 60° for 1 hour to convert the amine into its hydrochloride, and is then cooled in a freezing mixture, and an ice-cold solution of sodium nitrite (20 g. in 50 c.c. of water) is added, with vigorous stirring, during not less than 1 hour. The diazonium solution is filtered and added slowly to a solution of sodium sulphite, prepared by passing sulphur dioxide into a solution of 45 g. of sodium hydroxide in 300 c.c. of water until an acid reaction is just indicated by phenolphthalein. (An excess of sulphur dioxide must be avoided; otherwise tarry matters are produced on addition of the diazonium solution and the yield of hydrazine is greatly diminished.) The resulting bright orange solution is warmed to 60°, and made acid to litmus by the addition of concentrated hydrochloric acid (about 20 c.c.); the colour then changes to pale yellow. The solution is heated for about an hour, 100 c.c. of concentrated hydrochloric acid are added, and the mixture is allowed to cool. The hydrazine hydrochloride crystallises as a pulp of small needles, which are filtered off and recrystallised from dilute hydrochloric acid (1 : 4). The yield of the air-dried product is 80—90% of the theoretical.

Diketosuccinic acid 2 : 4-*dibromophenylosazone* (I) was prepared by adding a solution of 26 g. of sodium dihydroxytartrate (1 mol.) in 180 c.c. of moderately concentrated hydrochloric acid (1 : 1) to a fine suspension of 60 g. of 2 : 4-dibromophenylhydrazine hydrochloride (2 mols.) in 1500 c.c. of very dilute hydrochloric acid (1 : 100). The mixture was stirred for 6 hours and afterwards heated at 80° for 2 hours. The *osazone*, which separated as a soft, orange-coloured powder, was filtered off without previous cooling, repeatedly washed with boiling water, and dried at 110°. It was thus obtained as an orange powder, m. p. 205° (decomp.) (Found: Br, 50·1. $C_{16}H_{10}O_4N_4Br_4$ requires Br 49·8%).

Anhydrodiketosuccinic Acid 2 : 4-*Dibromophenylosazone* (II).—The osazone (I) was added to boiling acetic anhydride until no more would dissolve. A clear, deep red solution was thus obtained which on cooling deposited the *anhydride* in large, red, elongated prisms, m. p. 267° (decomp.) (Found: Br, 51·35. $C_{16}H_8O_3N_4Br_4$ requires Br, 51·3%).

1-2′ : 4′-*Dibromophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-2″ : 4″-*dibromophenylhydrazone* (III) is formed together with the isomeric anhydride (II) on crystallising the osazone (I) from acetic acid. The two isomerides are readily distinguished owing to their marked difference in colour and crystalline form. Their separation by crystallisation from acetic acid, although difficult on account of their sparing solubility, can be effected as follows: A saturated, boiling solution, during cooling to 70°, deposits most of (III) together with some of the anhydride; below this temperature, the anhydride continues to separate with only a small amount of the pyrazolone. By repeating the process with each of the two fractions the substances are obtained pure.

The compound (III) is, however, best obtained by acidifying the deep brown solution produced by boiling its ethyl ester (see below) (5 g.) for 4 hours with 200 c.c. of 10% sodium hydroxide solution; the orange-yellow powder thus obtained separates from acetic acid in clusters of minute, orange-yellow crystals, m. p. 248° (decomp.) (Found: Br, 51·4. $C_{16}H_8O_3N_4Br_4$ requires Br, 51·3%).

The *methyl* ester of the acid (III) is best obtained by heating the anhydride (II) in a sealed tube with methyl alcohol, containing 2% of dry hydrogen chloride, for 8 hours at 100°. It is moderately easily soluble in acetic acid, from which it separates in very small, orange-yellow needles, m. p. 233° (Found: Br, 50·2. $C_{17}H_{10}O_3N_4Br_4$ requires Br, 50·2%). The *ethyl* ester, obtained by boiling the osazone (I), the anhydride (II), or the pyrazolone (III) with alcohol containing 5% of dry hydrogen chloride, crystallises from acetic acid, in which it is moderately easily soluble, in long, slender, yellow prisms, m. p. 229° (Found: Br, 49·0. $C_{18}H_{12}O_3N_4Br_4$ requires Br, 49·1%). The n-*butyl* ester, which is similarly prepared, is easily soluble in acetic acid, from which it separates in yellow, glistening plates, m. p. 175° (Found: Br, 47·0. $C_{20}H_{16}O_3N_4Br_4$ requires Br, 47·1%).

Ethyl diketosuccinate 2 : 4-*dibromophenylhydrazone* (IV) is not readily obtained pure from ethyl diketosuccinate owing to the simultaneous formation of the osazone. It is, however, readily prepared from ethyl oxalacetate. A cold aqueous solution of 2 : 4-dibromobenzenediazonium chloride is added slowly and with vigorous stirring to an aqueous solution of the potassium derivative of ethyl oxalacetate, cooled in a freezing mixture. A sticky red mass separates from which, by repeated crystallisation from alcohol, the *hydrazone* is obtained in small, pale yellow, compact prisms, m. p. 95° (Found: Br, 35·4. $C_{14}H_{14}O_5N_2Br_2$ requires Br, 35·55%).

Ethyl diketosuccinate 2 : 4-*dibromophenylosazone* (V) cannot be prepared by the direct esterification of the osazone (I) on account of simultaneous pyrazolone formation. It is obtained by the action in alcoholic solution (1) of dibromophenylhydrazine upon the monohydrazone, (2) of excess of dibromophenylhydrazine upon ethyl diketosuccinate. It separates from alcohol in glistening, yellow, four-sided plates, m. p. 197° (Found: Br, 45·9. $C_{20}H_{18}O_4N_4Br_4$ requires Br, 45·8%). On boiling with alcohol containing hydrogen chloride, it is converted into the ethyl ester of (III), m. p. 229°, described above.

Diketosuccinic acid p-*bromophenylosazone* (I; $X = C_6H_4Br$) was obtained as a soft, orange-red powder, m. p. 201° (decomp.) (Found: Br, 33·2. $C_{16}H_{12}O_4N_4Br_2$ requires Br, 33·1%).

The *anhydride* (formula as II) forms deep red, compact prisms, m. p. 262° (decomp.) (Found: Br, 34·4. $C_{16}H_{10}O_3N_4Br_2$ requires Br, 34·3%). This and all the following compounds, unless otherwise stated, are moderately easily soluble in acetic acid, from which they were crystallised.

1-p-*Bromophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-p-*bromophenylhydrazone* (formula as III) is sparingly soluble in acetic acid, from which it separates in very small, compact, yellow prisms, m. p. 260° (decomp.) (Found: Br, 34·5. $C_{16}H_{10}O_3N_4Br_2$ requires Br, 34·3%).

Its *methyl* ester, which is best obtained by heating the osazone anhydride in a sealed tube with methyl alcohol, containing 2% of dry hydrogen chloride, for 8 hours at 100°, forms long, thin, orange prisms, m. p. 213° (Found: Br, 33·5. $C_{17}H_{12}O_3N_4Br_2$ requires Br, 33·3%). The *ethyl* ester forms thin, orange-yellow prisms, m. p. 191° (Found: Br, 32·5. $C_{18}H_{14}O_3N_4Br_2$ requires Br, 32·4%).

Diketosuccinic acid 2 : 4-*dichlorophenylosazone* (I; $X = C_6H_3Cl_2$) was obtained as a soft, orange-red powder, m. p. 198° (decomp.) (Found: Cl, 30·9. $C_{16}H_{10}O_4N_4Cl_4$ requires Cl, 30·6%).

The *anhydride* (formula as II) forms small, elongated, red prisms, m. p. 242° (decomp.) (Found: Cl, 31·9. $C_{16}H_8O_3N_4Cl_4$ requires Cl, 31·8%).

1-2′ : 4′-*Dichlorophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-2″ : 4″-*dichlorophenylhydrazone* (formula as III) is sparingly soluble in acetic acid, from which it separates in nodular aggregates of very small, yellow needles, m. p. 252° (decomp.) (Found: Cl, 31·7. $C_{16}H_8O_3N_4Cl_4$ requires Cl, 31·8%).

Its *ethyl* ester forms long, fine needles, m. p. 212° (Found: Cl, 29·9. $C_{18}H_{12}O_3N_4Cl_4$ requires Cl, 29·95%).

Diketosuccinic acid p-*chlorophenylosazone* (I; $X = C_6H_4Cl$) was obtained as a soft, orange-red powder, m. p. 195° (decomp.) (Found: Cl, 17·7. $C_{16}H_{12}O_4N_4Cl_2$ requires Cl, 18·0%).

The *anhydride* (formula as II) forms small, slender, red prisms, m. p. 257° (decomp.) (Found: Cl, 18·9. $C_{16}H_{10}O_3N_4Cl_2$ requires Cl, 18·8%).

1-p-*Chlorophenyl*-4 : 5-*diketopyrazoline*-3-*carboxylic acid* 4-p-*chlorophenylhydrazone* (formula as III) is obtained by crystallising the osazone from acetic acid. It is rather sparingly soluble in acetic acid, from which it separates in small, orange-yellow, compact prisms, m. p. 254° (decomp.) (Found : Cl, 18·8. $C_{16}H_{10}O_3N_4Cl_2$ requires Cl, 18·8%).

Its *ethyl* ester forms very slender, orange-yellow prisms, m. p. 190° (Found : Cl, 17·7. $C_{18}H_{14}O_3N_4Cl_2$ requires Cl, 17·5%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, March* 30*th*, 1927.]

CLXXXVI.—*The Solubility of Potassium Ferrocyanide in Water at Temperatures up to* 25°.

By REECE HENRY VALLANCE.

MANY investigators have attempted to determine the solubility of potassium ferrocyanide in water at various temperatures, but the results obtained, especially at lower temperatures, do not harmonise (see Vallance, *Chem. News*, 1922, **125**, 7). In the earlier investigations this may have been due in part to a variation in the purity or hydration of the ferrocyanide employed, or to inaccuracy in manipulation; but in recent work it appears more probable that the fault lies in the methods of estimating the amount of salt in the solution. It was deemed necessary at the outset to check the accuracy of the methods in general use, which are : (*a*) titration with potassium permanganate, (*b*) titration with a standard solution of a metallic salt, *e.g.*, of zinc or copper, and (*c*) decomposition of the ferrocyanide into hydrogen cyanide, absorption of the latter by potash, and titration with standard silver nitrate solution.

The first method has been most generally used in solubility determinations, although its accuracy has long been questioned. It does not give good results, since the colour due to a slight excess of the oxidising agent is not easily perceived, and none of the many modifications hitherto proposed was found to be entirely satisfactory.

The second method was not considered suitable for the work in view, since all estimations must be made under exactly similar conditions, and this would be difficult with a series of solutions of different concentrations, of which only limited quantities were available.

The method by which the ferrocyanide is decomposed with evolution of hydrogen cyanide has been used with fairly satisfactory results (Feld, *Chem. Zentr.*, 1903, ii, 1398; Colman, *Analyst*, 1908,

33, 261; 1910, **35**, 295), although it is found difficult to avoid loss of the acid (Skirrow, *J. Soc. Chem. Ind.*, 1910, **29**, 319; Williams, *ibid.*, 1912, **31**, 468). Williams showed that solutions of potassium ferrocyanide are catalytically decomposed when boiled with cuprous chloride in the presence of hydrochloric acid. By collecting the evolved acid in alkali, and afterwards titrating with standard silver nitrate, the ferrocyanide originally present may be estimated. This method appeared suitable for the work in view, and was therefore investigated. (The salt used throughout this research was the A.R. trihydrated potassium ferrocyanide, supplied by the British Drug Houses, Ltd.) Great care was taken to avoid loss of hydrogen cyanide, but a series of estimations gave results which were discordant to the extent of 7%, mostly low. In spite of the addition of potassium iodide, the end-point was determined only with difficulty, possibly because of the strong alkali present. Moreover, the method was inconvenient.

Attention was next directed to the method based on the decomposition of complex cyanides by persulphates in presence of mineral acids (Dittrich and Hassel, *Ber.*, 1903, **36**, 1929), 50% of the hydrogen cyanide being evolved and ammonium salts formed. The iron can then be precipitated by ammonia and estimated in the usual way. This method at first appeared satisfactory, but when it was applied to larger quantities (1—4 g.) of the ferrocyanide, the blue precipitate which formed when the acidified mixture of ferrocyanide and ammonium persulphate was heated could not be redissolved, even by the addition of hydrochloric acid and prolonged heating with excess of the persulphate. This method was used for solubility determinations by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2714), who admitted that, in spite of the fact that pure hydrogen was passed through the solutions to prevent oxidation, the formation of the blue precipitate sometimes either prevented or vitiated the analyses.

It was found to be impracticable to dry and weigh the ferrocyanide in the anhydrous condition: the loss of water, after heating for definite periods at 105—110°, was always lower than that required by the trihydrate formula, unless the partial decomposition, which was nearly always apparent, became very marked. It is probable, therefore, that the true loss of water would be still lower.

It was thought that it would be more satisfactory if the iron could be converted into the ferric condition, as was attempted in the persulphate method, and many experiments were made in which the salt was heated alternately with concentrated sulphuric acid and concentrated nitric acid. After such treatment, the residue on ignition did not yield a product of constant composition (*e.g.*,

$4K_2SO_4,Fe_2O_3$) and the silica crucibles used were badly attacked. The following method, however, gave excellent results and was used throughout for the solubility determinations.

The Estimation of Iron in Potassium Ferrocyanide.

A weighed quantity of potassium ferrocyanide in a platinum dish was just covered with concentrated sulphuric acid and heated (in a fume-chamber) very gently on a sand-bath until all action had ceased, and then strongly for about ½ hour. After cooling, a little more concentrated sulphuric acid and a few drops of concentrated nitric acid were added, and the heating was repeated, at first gently and then strongly until the residue was dry; this was then cooled, gently warmed with concentrated hydrochloric acid, transferred to a 500 c.c. beaker containing a little hot water, and diluted to about 300 c.c. with water; a few drops of concentrated nitric acid were added, and the mixture was gently boiled until a clear solution was obtained; this was allowed to cool, and made up to 500 c.c. in a flask which had been graduated against a 100 c.c. pipette.

For each estimation, 100 c.c. of the solution were withdrawn by means of this pipette, and the ferric hydroxide was precipitated from the hot solution by addition of ammonium hydroxide. The precipitate was washed several times by decantation, transferred to two filters (in order to facilitate washing), thoroughly washed with hot water until the filtrate was quite free from sulphate and chloride, dried at 110°, ignited, and weighed [Found, for different specimens: Fe, (i) 13·416, (ii) 13·397, (iii) 13·403. Calc. for $K_4Fe(CN)_6,3H_2O$: Fe, 13·22%].

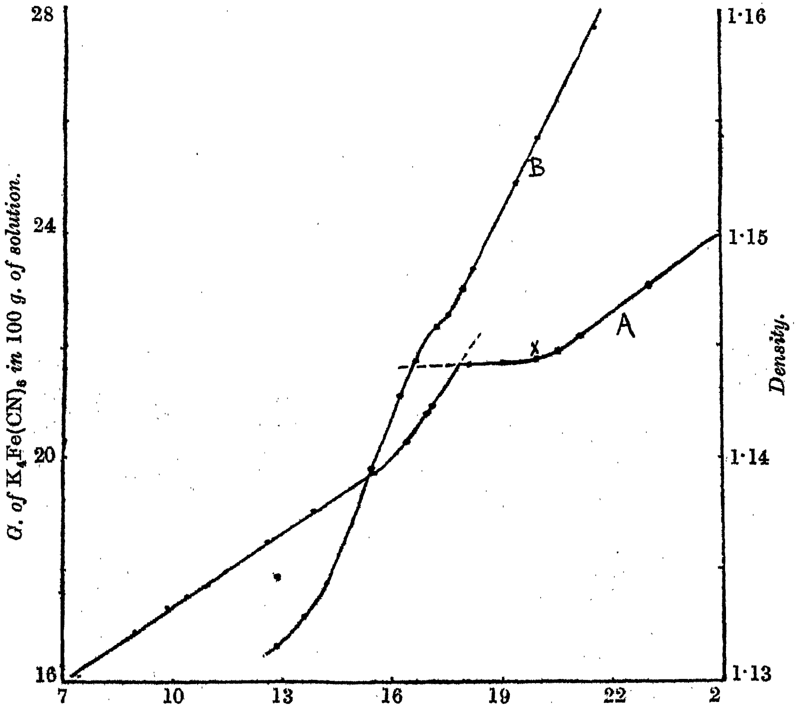
The results, although concordant, were higher than the value required by theory, and to a greater extent than can be accounted for by the low results obtained (p. 1329) for the loss of water on heating.

The method outlined above has also been employed by Friend and Merriman in this laboratory for the estimation of alkali ferricyanides, accurate results being obtained.

Determination of the Solubility of Potassium Ferrocyanide at Temperatures up to 25°.

The method employed was similar to that described by Lumsden (J., 1902, **81**, 350). The solution to be tested was constantly stirred in contact with the salt for about 7 hours, a portion then being drawn by suction from the saturation vessel, through a Gooch filter containing glass wool (previously washed and dried), into a receiving flask. The whole apparatus was sufficiently immersed in a thermostat for the solution to remain under water during the transference, a constant temperature being carefully maintained. A suitable quantity of the filtered solution was immediately weighed into a platinum dish, evaporated to dryness, and the residue decomposed by means of sulphuric acid and estimated by the method already described. The results are in Table I, where *s* represents g. of anhydrous salt in 100 g. of saturated solution. When these results are plotted as in Fig. 1, it is seen that the solubility curve is not continuous, but that a break occurs between 17° and 18°.

FIG. 1.



Temperature.

A. *Solubility curve.* B. *Density curve.*

[ˣ *Value obtained by Briggs* (loc. cit.) *for " a " salt.*]

TABLE I.

Temp.	*s.*	Temp.	*s.*	Temp.	*s.*	Temp.	*s.*
7·4°	16·043	12·6°	18·514	17·0°	20·922	* 23·1°	23·074
8·9	16·844	* 13·8	19·067	17·9	21·687	* 25·0	23·971
9·8	17·309	15·5	19·715	19·0	21·725		
* 10·4	17·541	16·3	20·240	* 20·4	21·953		
11·1	17·784	* 16·9	20·862	21·1	22·244		

* Vallance, *loc. cit.*

This points to a change in the solid phase, possibly due to a change in the degree of hydration, but it is of particular interest in view of the long-admitted possibility of the existence of two stereoisomeric forms of potassium ferrocyanide (Briggs, J., 1911, **99**, 1019; 1920, **117**, 1026; Bennett, J., 1917, **111**, 490).

The density of the saturated solution at different temperatures was next examined. A silica pyknometer of about 20 c.c. capacity was employed, and the slight change in capacity with rise in temperature was determined by weighing it full of mercury at two different temperatures. In order to fill the pyknometer with the saturated solution, it was attached to the receiving flask of the solubility apparatus whilst immersed in the thermostat, and the solution was drawn over by suction. The density was calculated from the formula

$$D^{t^\circ}_{4^\circ} = W(1-0\cdot0012/d)/C + 0\cdot0012,$$

where W = apparent weight of solution in air at t°, C = capacity of pyknometer at t°, d = density of water at t°, and 0·0012 = mean density of air.

The results are in Table II.

TABLE II.

Temp.	$D^{t^\circ}_{4^\circ}$.	Temp.	$D^{t^\circ}_{4^\circ}$.	Temp.	$D^{t^\circ}_{4^\circ}$.	Temp.	$D^{t^\circ}_{4^\circ}$.
12·8°	1·13153	16·2°	1·14295	17·9°	1·14789	21·5°	1·15811
13·7	1·13307	16·6	1·14441	18·2	1·14861	25·1	1·17041
14·2	1·13430	17·2	1·14596	19·5	1·15279		
15·4	1·13953	17·5	1·14641	20·0	1·15435		

Very few determinations have been made by previous workers, but those of Michel and Krafft (*Ann. Chim. Phys.*, 1854, **41**, 478), who give D^{15° = 1·1441, of Sonstadt (J., 1906, **89**, 343), $D^{8\cdot9^\circ}$ = 1·1191, and of Farrow (J., 1926, 49), $D^{24\cdot9^\circ}$ = 1·1731, are in general agreement with the above figures. The value obtained by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2714), D^{25° = 1·09081, is obviously incorrect. When the results are plotted as in Fig. 1, a slight change in the direction of the curve is observable above 17°.

In order, if possible, to detect an actual transition point, the dilatometric method was employed. The dilatometer contained *m*-xylene as the indifferent fluid, and the long stem was surrounded by the graduated tube of a burette which served as a scale and also protected the capillary from fluctuations of temperature. The instrument was immersed in a thermostat at a definite temperature, and after allowing 15 minutes for the apparatus to assume this temperature, the movement of the meniscus was observed.

For short periods of time there was no appreciable movement at any given temperature, but with longer periods the following results were obtained :

Temp.	Time (hrs.).	Variation in level of fluid.	Variation per hour.
29·3°	24	−0·60	−0·025
21·6	26·5	−0·55	−0·020
19·0	24	−0·35	−0·014
17·0	24	+0·20	+0·008
13·5	21	+0·50	+0·024

It will thus be seen that a simple interpolation gives the equilibrium temperature as 17·7°, which agrees with the transition point indicated by the break in the solubility curve.

The cooling curves of solutions of potassium ferrocyanide of various concentrations over the range 24—13° were found to be quite smooth.

The iron content of a number of samples of crystals, grown at 0° and at temperatures somewhat above 30°, has been determined. The crystals were dried for varying periods between absorbent material under a uniform pressure of 4 lb.; it was found that the composition remained constant after 24 hours. In all cases the results were the same, the iron content approximating to that required by the trihydrate. Further, no differences could be detected in the crystalline form of crystals grown at temperatures above and below the transition point; no crystallographic measurements have been made, however.

Table III shows the densities of the saturated solutions and the solubilities as interpolated at even temperatures.

TABLE III.

		G. of $K_4Fe(CN)_6$				G. of $K_4Fe(CN)_6$	
Temp.	$D_{4°}^{t°}$.	in 100 g. H_2O.	in 100 g. sol.	Temp.	$D_{4°}^{t°}$.	in 100 g. H_2O.	in 100 g. sol.
7·5°	—	19·19	16·10	*17·7°*	*1·1471*	*27·62*	*21·64*
10·0	—	21·00	17·36	20·0	1·1543	28·02	21·89
15·0	1·1378	24·25	19·52	25·0	1·1701	31·53	23·97

Summary.

1. Various methods of estimating alkali ferrocyanides have been critically examined, and a new process, involving the conversion of the ferrocyanide to the ferric condition by means of concentrated sulphuric and nitric acids, is described. This method is shown to be accurate and suitable for use in solubility determinations. It may also be used for the estimation of ferricyanides.

2. The solubilities of potassium ferrocyanide in water at temperatures up to 25° have been determined and represented by a curve.

A break in the latter indicates a change in the solid phase, the transition point being about 18°.

3. The densities of saturated solutions of the salt have been determined, and the density curve shows a slight change in direction above 17°.

4. By the dilatometric method, the transition point between the two phases is established at 17·7°.

5. Crystals of the salt grown above and below the transition point did not exhibit any apparent difference in crystalline form or in the degree of hydration.

The author wishes to express his indebtedness to Dr. J. Newton Friend for his constant help and interest in this research.

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[*Received, February 18th,* 1927.]

CLXXXVII.—*Selective Solvent Action. Part VI. The Effect of Temperature on the Solubilities of Semi-solutes in Aqueous Alcohol.*

By ROBERT WRIGHT.

THE formation of complexes between its constituents has frequently been assumed to account for the deviation of certain physical properties (*e.g.*, viscosity, refractive index, and density) of aqueous alcohol from those calculated from the mixture rule. If such solvates exist, then it may be expected that rise of temperature will decrease the extent of solvation, since, as a rule, complexes dissociate at higher temperatures. Such a decrease in solvation should affect the solvent power of the mixed solvent for a semi-solute. For example, if 50% aqueous alcohol at 100° contains a higher proportion of free (desolvated) alcohol and water than the same mixture at 20°, this increase in the amount of free water and alcohol should cause an increase in the solubility of a water-soluble salt, or of an alcohol-soluble organic substance. Such an increase in solubility is distinct from the ordinary increase in solubility which takes place in a simple solvent with rise of temperature. In Table I are given the solubilities of five salts (none of which crystallises with water of crystallisation) at 20° and at 100°, both in water and in 50% (by weight) aqueous alcohol. The ratio of the solubilities at the two temperatures is also given for each salt both in water and in the mixed solvent. It will be seen that the ratio is always greater for the mixed solvent than for pure water. If the extent of water–alcohol solvation remained the same at 100° as at 20° there would be the same proportion of free water at the two temperatures, and consequently the ratio of the solubilities of a salt at the two temperatures should be the same for the mixed solvent as it is for pure water. Since this ratio is always greater in the case of the aqueous alcohol, it is concluded that rise of temperature tends to decompose the water–alcohol complexes, this increase in free water producing the abnormal increase in salt solubility.

Table I.

Solubilities of salts in water and in 50% (by weight) aqueous alcohol at 20° and 100°.

(G. of solute per 100 g. solvent.)

	Water, 20°.	Water, 100°.	Ratio, 100°/20°.	50% EtOH, 20°.	50% EtOH, 100°.	Ratio, 100°/20°.
NaCl.	36·0	39·1	1·09	9·8	12·1	1·24
	36·0	39·1		9·8	12·1	
KCl.	34·3	56·5	1·64	6·0	15·3	2·55
	34·3	56·0		6·0	15·3	
$KClO_3$.	7·2	56·8	7·84	1·1	14·0	12·8
	7·2	56·0		1·1	14·2	
K_2SO_4.	11·1	23·9	2·15	0·15	0·51	3·64
	11·2	24·1		0·13	0·51	
$Ba(NO_3)_2$.	9·1	33·5	3·69	1·0	4·7	4·65
	9·1	33·6		1·0	4·6	

The solubilities of potassium nitrate in aqueous alcohol of varying composition at 20° and 60° are given in Table II, the values being taken from Seidell's solubility tables. The ratio of the solubilities at the two temperatures is given in each case and it will be seen that it is always greater for aqueous alcohol, of whatever composition, than for pure water. Judging from the values of the ratios, the desolvation with rise of temperature would seem to be greatest with alcohol of about 20% strength. It is obvious that aqueous alcohol which contains only a small proportion of one component, whether alcohol or water, will on desolvation only slightly alter the amounts of its free constituents. Hence the values of the ratios for 90% alcohol and for 5% alcohol are nearer the ratio given by pure water than are those for alcohol–water mixtures of intermediate strength.

Table II.

Solubility of potassium nitrate in aqueous alcohol of various concentrations.

(G. per 100 g. solvent.)

Alcohol, %	0	5·5	9·4	13·6	19·1	30	40	60	90
20°	31·6	24	20	16	11	7	5	2	0·3
60°	110	93	79	69	52	31	21	8	1·1
Ratio	3·48	3·87	3·95	4·31	4·72	4·43	4·20	4·00	3·67

For alcohol-soluble solutes, the same result was obtained, but here it was necessary to take into consideration the solubility of the substance in water, which was never negligible, and, in the case of succinic acid, was comparable with that in alcohol. In Table III are given the solubilities at 20° and 30° of four substances in water, alcohol, and the 50% mixture. The ratio of the solubilities at the two temperatures is also given in each case both for the mixed and for the unmixed solvents; with the unmixed solvents the sum of the solubilities is used in calculating the ratio. Again it will be seen that the increase of solubility is always greater with the mixed solvent.

It is thus obvious that a considerable amount of desolvation of the aqueous alcohol takes place with rise of temperature, although it is not possible to calculate the exact extent of such a change. It is, however, not complete at 100°, for in such an event the alcohol would have no effect on the solvent power of water, and the solubility of a salt in 50% alcohol would be simply half of its solubility in pure water.

TABLE III.

Solubilities of some organic substances in water, alcohol, and 50% (by weight) aqueous alcohol, at 20° and 30°.

(G. of solute per 100 g. solvent.)

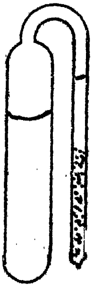
At 20°.

Solvent.	Succinic acid.	Benzoic acid.	Salicylic acid.	Acetanilide.
Water.	6·8	0·34	0·21	0·53
	6·7	0·35	0·23	0·52
Alcohol.	10·0	53·0	51·0	28·8
	10·1	52·0	52·0	28·8
50% EtOH.	13·6	17·0	11·8	11·9
	13·8	16·9	11·8	11·9
At 30°.				
Water.	10·5	0·41	0·30	0·70
	10·4	0·43	0·32	0·72
Alcohol.	12·0	66·0	57·0	40·7
	11·8	65·6	57·5	40·3
50% EtOH.	20·8	25·4	17·9	18·9
	21·0	25·0	18·0	18·7
Ratios of solubilities, 30°/20°.				
Unmixed solvents.	1·33	1·25	1·11	1·42
Mixed solvents.	1·52	1·48	1·52	1·58

EXPERIMENTAL.

The solubilities at 20° and 30° were determined in the usual manner. The saturated solutions were prepared in stoppered tubes in a thermostat, weighed portions were taken, and the amount of solute was estimated either by titration or by evaporation to dryness. In the case of acetanilide, the evaporation was carried out under reduced pressure at 40°. At 100°, in addition to the usual necessity of obtaining a saturated solution free from excess of suspended solute, care had to be taken to guard against alteration in the composition of the mixed solvent by evaporation. The method of carrying out a determination was as follows. To a test-tube of 10 mm. diameter and 5 c.c. capacity was sealed a 20 cm. length of tubing about 4 mm. in diameter. After cleaning and drying, a sufficient quantity of dry salt was placed in the tube and about 3 c.c. of solvent were added by means of a pipette, care being taken to avoid wetting the walls of the narrower tube. This tube was then bent round until it lay parallel with the test-tube (see Fig. 1), and was finally sealed off as shown, the whole forming a U with one limb wider than the other. The sealed tube was rocked in a bath at 100° for 4 hours until saturation was complete. It was then held in a special pair of tongs, and, while still under the boiling water, was manipulated so that the excess solid was brought into the narrow limb, the wide limb being left about three-quarters full of the clear saturated solution. The tube was now removed from the bath and allowed to cool to room temperature; part of the salt crystallised during the cooling, but as the tube was sealed no alteration in the composition of the solvent could take place. The wide limb was cut off above the level of the solution and weighed with its contents, and the solubility of the salt was found by evaporation to dryness and a second weighing.

FIG. 1.



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[*Received, July 22nd,* 1926.
Amplified, May 14th, 1927.]

CLXXXVIII.—*The System Lead Chloride–Lead Iodide–Water.*

By ARTHUR LINDSAY MCRAE SOWERBY.

THE literature yields only the most conflicting and unsatisfactory accounts of double salts of the type $x\mathrm{PbCl_2},y\mathrm{PbI_2}$, and a systematic investigation of their stability and properties was therefore undertaken.

Various workers (*e.g.*, Dietzell, *Dingler's Poly. J.*, 1868, **190**, 41; Field, J., 1893, **63**, 540) have prepared salts to which they ascribed formulæ of this type, without sufficient evidence that they were true double salts. Herty (*Amer. Chem. J.*, 1896, **18**, 290) claims to have shown that these substances were not true chemical compounds, but isomorphous mixtures of lead chloride and lead iodide; and later (Herty and Boggs, *ibid.*, 1897, **19**, 820), he concluded that "all the evidence thus far obtained tends to show that lead iodide and lead chloride will crystallise together, the lead chloride being in excess."

Thomas (*Compt. rend.*, 1898, **126**, 1349), reviewing previous work in conjunction with his own, concluded that PbICl could exist as a true compound.

Two-component Systems.

To the system lead iodide–lead chloride–water there correspond three two-component systems, *viz.*, each salt and water, and the two salts only. The first two systems show no points of particular interest within the temperature range over which they have been investigated (0—100°); in neither case is there any report of a hydrate, and the solubility is sufficiently small to make the temperature of the eutectic point approximate closely to that of pure water. At high temperatures, there is considerable hydrolysis, however, and the two-component systems lead chloride–water and lead iodide–water become special cases of the three-component systems lead oxide–water–hydrochloric or hydriodic acid, the solubility curves really representing the locus of the isothermal invariant points where lead hydroxide or a basic salt exists as a solid phase beside the normal salt.

The binary system lead iodide–lead chloride was investigated by Mönkemayer (*Neues Jahrbuch für Mineralogie*, Beilageband, 1906, **22**, 1) who concluded that it belonged to Roozeboom's Type V of mixed crystals (Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 403). The evidence upon which he based this conclusion appears to be insufficient; he observed the rate of cooling of fused mixtures of the two salts, and by plotting the time of the eutectic halt against composition, and extrapolating to zero eutectic halt, he obtained values for the limiting compositions of the mixed crystals. On re-plotting the figures given by Mönkemayer and extrapolating as described, the limiting compositions appear to be 100% $PbCl_2$ and 100% PbI_2, respectively. There is no other evidence in the paper of the formation of mixed crystals, nor is any compound formed at these temperatures. It is therefore very doubtful whether the relations are not those of the simplest possible two-component system—two melting-point curves meeting in a eutectic point at 306°.

EXPERIMENTAL.

All results were obtained by the analysis of solutions and solids which had been allowed to attain equilibrium in a thermostat; the analysis normally comprising a volumetric estimation of total halides by Volhard's method and an independent estimation of iodide by another method. Since in all cases the concentration of chloride was high compared with that of iodide, the errors in determining the former by difference are not appreciably greater than if the chloride had been directly determined.

Determination of Iodide.—The determination of the iodide in presence of a large excess of chloride offered considerable difficulty, especially as the concentration of lead iodide never exceeded 0·09 g. per 100 c.c. of solution (corresponding to less than 0·05 g. of iodine per 100 c.c.).

Of the many methods tried and abandoned, two only are of interest. The first depends upon the statement of Pisani (Fresenius, "Quantitative Analysis," Sixth Ed., 444) that if silver nitrate solution be run into a solution containing mixed iodides and chlorides to which have been added a few c.c. of starch iodide solution of known silver value, the metallic iodide is first precipitated, and next the iodine from the starch iodide, thus giving an end-point before the chlorides begin to be precipitated. On trial with very dilute solutions, using the equivalent of 0·05 c.c. of *N*/10-solution of iodide for each titration and *N*/1000-silver nitrate, it was found that this statement is correct, provided that the chloride concentration is not much greater than that of the iodide. In the presence of a large excess of chloride, however, the end-point was delayed, the quantity of silver nitrate required increasing by about 40% as the chloride concentration was increased up to about 100 times that of the iodide. For analysis of the solutions in the present work, this method was therefore valueless, but it was found convenient for the analysis of the solids, of which only small amounts were available. Trustworthy results were obtained, provided that (*a*) the normality of the chloride was not more than double that of the iodide, (*b*) the total volume of the solution being titrated was kept constant in all cases, and (*c*) the silver nitrate solution was standardised against an iodide solution of known concentration under operating conditions.

The second method that proved unsuccessful in its original form is due to Benedict and Snell (*J. Amer. Chem. Soc.*, 1903, **25**, 1139); in this method, the iodine is liberated by iodate and acetic or nitric acid, and extracted with carbon disulphide. The resulting pink solution is washed and titrated with thiosulphate. Three difficulties, all due to the extreme smallness of the amount of iodide to be measured, were encountered:

(*a*) The acetic acid available (ordinary laboratory reagent) appeared to re-absorb, by some secondary reaction, the iodine at first liberated, so that the results obtained depended on the length of time that elapsed between the liberation and the final extraction, and were invariably low, although not by a constant amount. Nitric acid of ordinary purity was free from this objection, and was consequently used for further experiments.

(*b*) The carbon disulphide used reacted with iodine slowly, the titration value of the solution falling to about one-half in 15 hours, but carbon tetrachloride proved to be satisfactory and was used throughout.

(*c*) The very dilute solution (approx. 0·005N) of thiosulphate used gave erratic variations of the order of 20% in the titrations. Every attempt to eliminate this source of error failed completely, and solutions of arsenious oxide gave rise to similar variations.

Finally, a colorimetric method, based on the method of Benedict and Snell, was adopted: Ten c.c. of the solution to be examined were diluted with a little water to prevent crystallisation, and the lead was precipitated as sulphate and filtered off. Filtrate and washings were made up to 300 c.c. in a separating funnel. A known volume of a standard lead iodide solution was made up to the same volume in a second funnel. The iodine was then liberated in both funnels by the addition of potassium iodate and nitric acid, extracted with carbon tetrachloride, and the two resulting solutions were made up to the same volume in small standard flasks. These solutions were then matched in a Dubosc colorimeter, illuminated preferably by daylight. From the colorimeter readings and the known concentration of one solution, that of the other could readily be calculated. This method was found to be accurate to within 2%, even in estimating no more than 0·5 mg. of iodine.

Results.

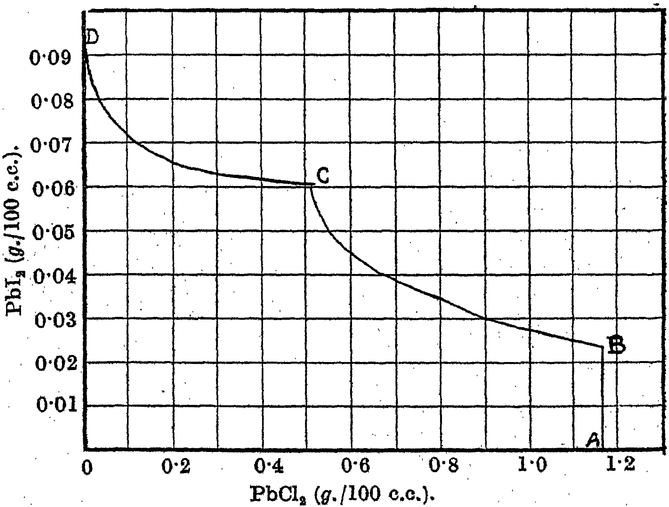
Table I and Fig. 1 summarise the results obtained at 30°. The letters in the first column of the table refer to the corresponding points in the diagram. The points B and C are isothermal invariant points. The continuity of the curve BC is evidence of the existence of only one solid over this range of concentrations. Analysis of the solid obtained from solutions represented by the curve BC was attempted, but the quantity obtained was so small as to preclude accuracy.

In order to obtain larger quantities of this solid, the necessary quantities of lead iodide and lead chloride were boiled with water until they dissolved, and the solution was allowed to come to equilibrium in the thermostat. A sample of the solution was then withdrawn and analysed for total halides in order to determine with sufficient accuracy the point on the curve to which the solution

TABLE I.

	Solution.		
	PbI_2 (g./100 c.c.).	$PbCl_2$ (g./100 c.c.).	Solid phase.
A.	—	1·171	$PbCl_2$
	0·0081	1·171	,,
	0·0120	1·171	,,
	0·0168	1·171	,,
B.	0·0235	1·171	$PbCl_2$ & PbICl
	0·0241	1·140	PbICl
	0·0277	0·969	,,
	0·0278	0·958	,,
	0·0334	0·820	,,
	0·0390	0·717	,,
	0·0421	0·631	,,
	0·0432	0·631	,,
	0·0520	0·550	PbICl
	0·0531	0·545	,,
C.	0·0602	0·518	PbICl & PbI_2
	0·0606	0·417	PbI_2
	0·0620	0·352	,,
	0·0630	0·270	,,
	0·0647	0·209	,,
	0·0687	0·144	,,
	0·0712	0·100	,,
	0·0788	0·046	,,
D.	0·091	—	,,

FIG. 1.



System $PbCl_2$–PbI_2–H_2O.

corresponded. Larger amounts of solid, often as much as 0·5 g., were thus obtained. These solids were analysed, after drying, by Volhard's method for total halides, and by Pisani's method (see above) for iodide. As a check, chlorides were estimated again after liberating and boiling off the iodine. No attempt was made to estimate lead in the solid, since the boiling involved in its preparation caused a small amount of basic salt to be formed. The results are summarised in Table II, and it is seen that the solid in equilibrium with solutions having the concentrations expressed by the curve BC is PbICl. No other compounds are formed at this temperature.

TABLE II.

Solution.		Solid.		
$PbCl_2$ (g./100 c.c.).	PbI_2 (g./100 c.c.).	$PbCl_2$ (equivs./100 g.).	PbI_2 (equivs./100 g.).	Ratio $PbI_2 : PbCl_2$.
0·86	0·032	0·271	0·265	0·978
0·765	0·036	0·268	0·269	1·004
0·67	0·041	0·270	0·271	1·004
0·56	0·051	0·269	0·268	0·996

A line drawn from the origin of Fig. 1 through the points corresponding to solutions containing lead iodide and chloride in equimolecular quantities does not cut the solubility curve, BC, of lead chloroiodide, but the curve CD. In accordance with this, it is found that the double salt is decomposed by water at the temperature of the isotherm.

An attempt was made to determine the isotherm for 70°, but hydrolysis was so considerable that the work was abandoned.

Summary.

The isotherm for 30° in the system lead chloride–lead iodide–water has been completely investigated. Three solubility curves have been found, corresponding to the two salts and to the binary compound PbICl. This salt has been shown to be decomposed by water, and the composition of solutions with which it can remain in equilibrium has been determined.

Methods have been developed by which small amounts of iodide can be estimated in presence of chloride.

The author's thanks are due to Professor F. G. Donnan for his kindly interest in the work, and to the late Miss K. A. Burke for many valuable suggestions in connexion with methods of analysis.

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[*Received, April 7th*, 1927.]

CLXXXIX.—*The Ternary System Barium Iodide–Iodine–Water and the Formation of Polyiodides.*

By A. C. D. RIVETT and JOHN PACKER.

VARIOUS attempts have been made to define the equilibrium relations existing between polyiodides and their constituents and to assign formulæ to the former. That a tri-iodide, such as that of potassium or barium, may exist in solution is very generally assumed.

Clark and Duane (*Physical Rev.*, 1922, **20**, 85), in fact, claim to have made a detailed examination by *X*-ray methods of the crystal structure of potassium tri-iodide, but they do not state how the salt was prepared. Many others have failed to obtain it: neither from aqueous solution (Parsons and Whittemore, *J. Amer. Chem. Soc.*, 1911, **33**, 1933) nor from 60 or 40% alcoholic solutions (Parsons and Corliss, *ibid.*, 1910, **32**, 1367) can any solid polyiodide of potassium be isolated. From thermal examination of the binary system potassium iodide–iodine, Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1081) concluded that KI_4, highly dissociated, existed in the fusion, but they could find no evidence for the presence of a polyiodide poorer in iodine. According to Abegg and Hamburger (*Z. anorg. Chem.*, 1906, **50**, 403), no polyiodide of potassium of less complexity than KI_7 exists.

Pearce and Eversole (*J. Physical Chem.*, 1924, **28**, 245) obtained results in dilute solutions of barium iodide, unsaturated with iodine, which were fairly consistent with a supposition of the presence of tri-iodide; but in *M*-solutions and upwards, saturated with iodine, they considered that pentaiodide was formed. From measurements of conductivities, viscosities, migration numbers, distribution coefficients, and other properties, usually over very limited ranges of concentration, other authors have obtained indications of polyiodides to which, on more or less satisfactory grounds, they have been able to assign formulæ.

In order to obtain quantitative information over a much wider range of temperature and concentration of components than has yet been recorded, the system barium iodide–iodine–water has been investigated between − 15·8° and 90°. Barium iodide (B.D.H.), recrystallised from water as the hydrate $2BaI_2,15H_2O$, and lower hydrates obtained by heating, were used with resublimed iodine (A. R.) and water in the preparation of suitable complexes. These were rotated in sealed tubes in a thermostat at the required temperature from 0° to 90° until equilibrium was attained. Shorter times, with only intermittent stirring and shaking, were given at − 15·8°, the temperature being maintained by means of ammonium chloride and ice. Solutions were drawn off into pipettes through cotton-wool plugs, any iodine removed by reaction with the cotton being negligible. Iodine was estimated by direct titration of one sample with thiosulphate, whilst in another sample, from which the iodine had been completely removed by evaporation, the iodide was estimated volumetrically against silver nitrate with thiocyanate as indicator. At 0° and 25° the usual "rest" method was employed to give information as to the composition of the solid phase. At lower and higher temperatures the wet solid was not readily separated without alteration of composition. The initial complex was therefore carefully synthesised and its composition used instead. Provided that the complex is not very near in composition to the saturated solution, this method is fairly accurate.

Table I contains the results at 0° and 25°, and Table II those at − 15·8°, 50°, 75·2°, and 89·9°. Compositions are given in % by weight, those of water (not given) being obtainable by difference. In the last column hydrates are specified by figures in parentheses, giving first the number of barium iodide molecules, and secondly the number of water molecules.

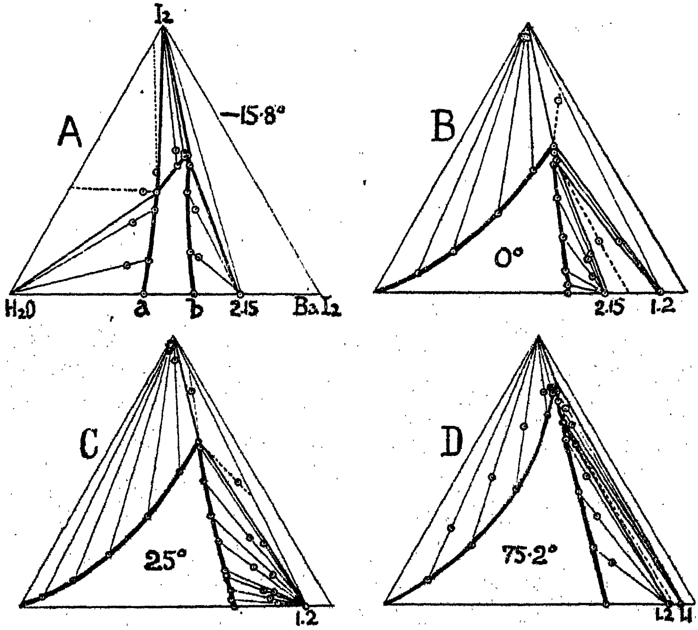
TABLE I.

Composition, % by weight.

		Solution.		Wet solid.		
Temp.	$D^{t^\circ}_{4^\circ}$.	BaI_2.	I_2.	BaI_2.	I_2.	Solid phases.
0° ± 0·05°	1·169	10·5	7·4	0·6	94·9	Iodine.
	1·365	17·9	15·2	1·1	94·6	"
	1·780	25·5	29·5	1·8	94·7	"
	2·415	29·0	45·4	3·0	94·1	"
	—	31·4	54·0	24·3	71·0	Iodine and (1, 2).
	—	32·7	51·8	69·8	19·0	(1, 2).
	—	34·6	49·4	63·0	19·2	(1, 2) and (2, 15).
	—	35·1	47·7	62·8	14·2	(2, 15).
	2·561	41·7	35·1	62·7	12·5	"
	2·322	50·4	20·3	66·9	6·2	"
	2·167	57·7	8·2	72·3	1·0	"
	2·108	60·7	3·0	72·2	0·5	"
	2·071	62·5	0·0	—	—	"
25° ± 0·02°	1·081	5·8	3·7	0·1	96·7	Iodine.
	1·214	12·4	10·0	0·4	97·3	"
	1·436	19·3	19·5	1·2	94·6	"
	1·827	24·8	33·2	1·5	96·3	"
	—	26·6	50·0	4·9	90·8	"
	—	27·2	61·1	16·3	79·7	Iodine and (1, 2).
	—	27·6	60·9	47·3	45·9	" "
	—	28·8	58·6	66·8	23·4	(1, 2).
	—	36·4	46·8	61·4	25·3	"
	—	44·8	33·8	75·6	11·5	"
	—	52·0	24·0	68·0	14·2	"
	2·405	59·7	13·3	78·9	5·2	"
	—	60·6	11·7	75·0	6·2	"
	2·339	64·3	6·5	78·5	3·1	"
	2·31	66·7	2·7	82·8	0·9	"
	2·277	68·8	0·0	—	—	"

From these tables and the triangular diagrams, the succession of changes may readily be followed. At − 15·8° (Fig. 1A) there are three curves, the solids being ice, iodine, and the hydrate (2, 15). At − 33·5°, the eutectic temperature of the binary system barium iodide–water (Packer and Rivett, J., 1926, 1061), the points *a* and *b* coincide, and below it all liquid phases are ternary in composition. A little below 0° the hydrate (1, 2) appears, and there are then four solubility curves. At 0° (Fig. 1B) the ice curve vanishes and the system is one showing three solids, iodine, (1, 2), and (2, 15). The latter hydrate cannot exist above 25·7°, and for a considerable temperature range beyond this the system is a simple one of two curves, as in Fig. 1C, the solids being iodine and (1, 2). Actually at 25°, for which this figure holds, there must be still a very small curve of (2, 15), but this has been omitted. The relations between compositions of solutions and "rests" at 25° give proof that the highest hydrate is (2, 15), and not either (1, 7) or (1, 6), as has been commonly assumed (compare Packer and Rivett, *loc. cit.*, p. 1062).

FIG. 1.



The temperature at which the hydrate (1, 1) first occurs in the ternary system could not be determined accurately by the thermometric method, but at 75·2° its solubility curve is as shown in Fig. 1D: that of (1, 2) vanishes at 98·9°.

Apart from the fact that no solid polyiodide is obtained, the interest of the system lies in the solubilities attained by iodine. In Table III are set out figures for the iodine saturation curves, compositions of solutions being given in equivalents per 1000 g. of water. In the last column is given the ratio of iodine atoms to iodide ions in solution. The amount of combined iodine is presumably the total found by titration with thiosulphate less that merely dissolved in the water. The amount of the latter cannot be

TABLE II.

Composition, % by weight.

	Solution.		Initial complex.		
Temp.	BaI_2.	I_2.	BaI_2.	I_2.	Solid phases.
−15·8° ± 0·1°	43·5	—	—	—	Ice.
	38·7	12·7	32·5	10·6	,,
	31·4	31·3	26·7	26·8	,,
	28·5	37·6	24·3	38·2	Ice and iodine.
	28·7	37·6	24·9	45·4	,, ,,
	30·8	47·5	27·1	53·3	Iodine.
	31·2	50·8	30·2	52·5	,,
	32·2	51·4	34·6	47·8	Iodine and (2, 15).
	38·7	37·6	44·4	31·4	(2, 15).
	50·4	15·9	54·1	13·5	,,
50° ± 0·02°	11·0	10·1	8·1	24·6	Iodine.
	19·9	24·9	14·3	42·2	,,
	24·5	47·2	18·6	57·2	,,
	22·1	68·3	21·5	69·4	,,
75·2° ± 0·05°	9·4	9·8	7·4	28·5	Iodine.
	17·0	23·0	11·6	47·0	,,
	21·4	42·5	12·7	65·6	,,
	18·0	70·0	12·8	78·5	,,
	15·7	77·6	14·1	79·8	,,
	14·3	82·0	—	—	Iodine and (1,1) (extrap.).
	16·8	78·3	22·6	72·4	(1, 1).
	18·9	74·9	27·2	66·3	,,
	24·2	67·2	32·2	59·3	(1, 1) and (1, 2).
	28·6	60·7	42·1	47·4	(1, 2).
	41·8	41·6	52·3	32·7	,,
	56·6	21·0	65·3	15·7	,,
89·9°	12·8	83·4	8·9	88·0	Iodine.
	14·7	75·3	9·7	83·2	,,

TABLE III.

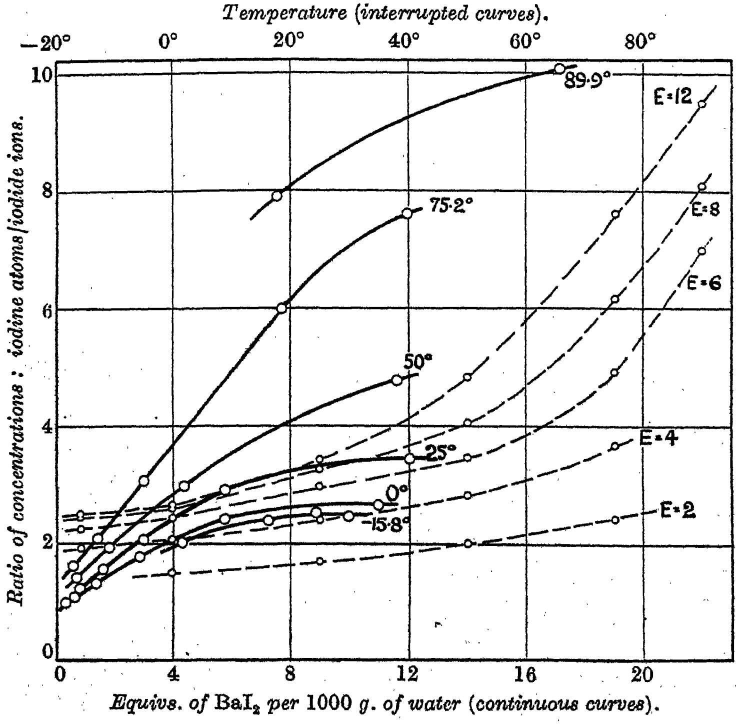
(Solutions saturated with iodine.)

	Equivs. per 1000 g. H_2O.				Equivs. per 1000 g. H_2O.		
Temp.	BaI_2.	I_2.	Ratio $I_2 : BaI_2$.	Temp.	BaI_2.	I_2.	Ratio $I_2 : BaI_2$.
−15·8°	4·35	8·79	2·02	50°	0·70	1·00	1·42
	7·27	17·28	2·38		1·84	3·54	1·93
	8·88	22·28	2·51		4·42	13·13	2·97
	9·99	24·59	2·46		11·65	55·5	5·55
0°	0·65	0·71	1·09	75·2°	0·59	0·95	1·61
	1·37	1·79	1·31		1·45	3·02	2·08
	2·90	5·16	1·78		3·04	9·29	3·06
	5·79	13·97	2·41		7·71	46·2	5·99
	11·0	29·1	2·65		11·98	91·3	7·62
25°	0·33	0·32	0·98	89·9°	7·52	59·3	7·9
	0·82	1·015	1·24		17·2	173·0	10·1
	1·61	2·51	1·56				
	3·02	6·23	2·06				
	5·81	16·84	2·90				
	12·08	41·4	3·43				

accurately estimated without making more or less arbitrary assumptions: in any case it will be small compared with the total iodine concentrations in the cases examined.

Fig. 2 contains two sets of curves which illustrate these results. The continuous lines are isotherms showing the ratio of iodine atoms to iodide ions plotted against equivs. of iodide per 1000 g. of water. At first they are not far from straight lines, but later they flatten, and at the lower temperatures seem to reach maxima. Throughout, the more iodide present, the more iodine is taken up per equiv. of iodide. In very dilute solutions at all temperatures the ratio of atoms to ions approximates to unity (compare Pearce and Eversole, *loc. cit.*, p. 252), and then with increase of salt concentration it rises the more rapidly the higher the temperature. From these curves have been obtained by interpolation the values of the ratio of atom to ion at different temperatures for barium iodide concentrations of 2, 4, 6, 8, and 12 equivs. per 1000 g. of solvent, and in Fig. 2 the interrupted curves show for each of these concentrations the values of the ratios plotted against temperature. The higher the temperature the more iodine is added per equiv. of iodide, and the rate of increase is greater the greater the iodide concentration. Supposing all the iodine to be distributed evenly amongst the iodide

FIG. 2.



radicals, the composition of the polyiodide radical ranges from I_2' to I_{11}', and at temperatures above the highest investigated, 89·9°, still greater amounts of iodine would certainly be taken up.

Attempts to apply the mass action law in systems like these cannot be expected to succeed; and there seems no reason to suppose that the formation of any one polyiodide represents the sole action at any particular stage. A glance at the continuous curves of Fig. 2 shows how in the less concentrated solutions of barium iodide the ratio of iodine to iodide approximates to 2, corresponding with an ion I_3'. Over selected ranges of iodide concentration one can interpret the results in terms of this or of numerous higher polyiodides.

It is clear that iodination is progressive, increasing in extent per iodide ion with increase of concentration of the latter and with rise of temperature. Whether the temperature effect is due solely to increase of concentration, and hence mass effect, of the iodine in the water present, cannot be stated. One might expect a polyiodide to become more unstable and to dissociate with rise of temperature. It may be that the apparent increase of stability with rise of temperature is due to the fact that the formation of polyiodide is not an addition of iodine molecules to a simple iodide ion, I′, but is a replacement by iodine of the water molecules which the simple ion may attach to itself in numbers sufficient to constitute it a full co-ordination complex. Thus we should have

$$I',xH_2O + yI_2 \rightleftharpoons I',(x-y)H_2O,yI_2 + yH_2O.$$

If hydration and iodination of the ion are both exothermic reactions, but the former more so than the latter, rise of temperature will displace the equilibrium to the side of the latter, other things being equal. In dilute solution the tendency would be for the reaction to go to the left.

Summary.

1. The ternary system barium iodide–iodine–water has been fully examined at – 15·8°, 0°, 25°, and 75·2°, and partially at 50° and 89·9°.

2. The hydrate $2BaI_2,15H_2O$ has been shown to exist, but neither a hexa- nor a hepta-hydrate has been found. No solid polyiodides have been formed.

3. Assuming the iodine present in solution to be attached to the anion, the mean compositions of the polyiodides present in the solutions examined range up to $BaI_2,10I_2$ at 90°; and at higher temperatures the iodine content will be still greater.

4. For a constant water content of solution, the ratio of iodine to iodide increases with increase of iodide concentration; it also

increases with temperature for a constant iodide concentration. Both facts are explicable if the action be regarded as a replacement of water in a hydrated iodide ion by iodine, the heat of reaction of a simple ion with water being greater than that with iodine, so that the substitution of the latter for the former is endothermic.

UNIVERSITY OF MELBOURNE. [*Received, April 11th,* 1927.]

CXC.—*The Union of Benzoylacetonitrile with Organic Bases in the Presence of Salicylaldehyde. Part I.*

By PANCHAPAKESA KRISHNAMURTI and BIMAN BIHARI DEY.

SALICYLALDEHYDE and benzoylacetonitrile condense together in the presence of a few drops of piperidine to give a poor yield of 3-benzoylcoumarin (Krishnamurti and Dey, *Proc.* 13*th Ind. Sci. Cong.*, 1926); at the same time there is produced a *base*, $C_{14}H_{18}ON_2$. This base is obtained in good yield when piperidine and benzoylacetonitrile react together in molecular proportion in the presence (but not otherwise) of a few drops of salicylaldehyde. It is a mono-acid base which is stable towards mineral acids, with which it forms characteristic, crystalline salts, and towards boiling dilute aqueous alkalis, but is decomposed by alcoholic potash with the liberation of piperidine. It is converted into piperidine and benzoic acid by the action of alkaline permanganate.

No definite acetyl or benzoyl derivative could be prepared, but the base readily yields a *nitroso-hydrochloride* with hydrochloric acid and sodium nitrite, which is decomposed by sodium bicarbonate to give a bright yellow iso*nitroso*-derivative. This compound readily yields diacyl derivatives, and gives benzoic acid on distillation with 70% sulphuric acid. The original base, when heated above its m. p., is decomposed into its constituents.

That it is the *N*-hydrogen atom of piperidine that takes part in the reaction is shown by the fact that the *N*-alkylpiperidines do not give this reaction. The constitution of the base may therefore be represented by (I) $\mathrm{CH_2Bz{\cdot}C(:NH){\cdot}NC_5H_{10}}$ or (II) $\mathrm{CH_2Bz{\cdot}C{\vdots}NH{\cdot}NC_5H_{10}}$. Formula (II) is more in accordance with the properties of the base, especially its instability towards heat and its stability towards concentrated acids and towards alkalis. The *iso*nitroso-derivative may be represented thus: (III) $\mathrm{OH{\cdot}N{:}CBz{\cdot}C{\vdots}NH{\cdot}NC_5H_{10}}$.

The action of salicylaldehyde as catalyst may be explained by assuming that it first condenses with benzoylacetonitrile in the presence of piperidine to form the salicylidene derivative; the nitrogen atom of the CN group in this then reacts additively with piperidine by migration of the hydrogen atom of the NH group of the latter; finally, the compound thus produced is hydrolysed, salicylaldehyde being regenerated.

Nitro-, bromo-, and *p*-methoxy-salicylaldehydes—and also β-naphtholaldehyde, but to a lesser extent—similarly act as catalysts, whereas the reaction fails with *o*-methoxybenzaldehyde and *m*- and *p*-hydroxybenzaldehydes, which do not contain the necessary hydroxyl group in the ortho-position to the aldehyde group.

EXPERIMENTAL.

The Base (II).—A mixture of benzoylacetonitrile (1 mol.), piperidine (2 mols.), salicylaldehyde (2—3 drops), and absolute alcohol (50 c.c.) was heated under reflux for about 3 hours. A portion of the alcohol was then distilled off, and the reddish-brown solution was diluted with much water, mixed with concentrated hydrochloric acid (5 c.c.), and, after 12 hours, decanted from the resinous matter and treated with excess of sodium hydroxide. The thick, white precipitate, after being washed, crystallised from alcohol in colourless, rectangular prisms, m. p. 173° (yield, about 80%). The base is insoluble in water, ether, or petroleum, and easily soluble in benzene, alcohol, acetone, chloroform, or dilute acids; from the last it is precipitated unchanged by alkalis (Found: C, 72·85; H, 8·0; N, 12·2. $C_{14}H_{18}ON_2$ requires C, 73·0; H, 7·8; N, 12·2%).

When heated, the base first melted to a clear liquid and then boiled, piperidine being evolved; the residue was charred and insoluble in acids.

A suspension of the base (0·5 g.) in 2% sodium hydroxide solution (50 c.c.) was slowly treated with potassium permanganate (3 g.); subsequent boiling produced a copious evolution of piperidine. The liquid, after being concentrated and acidified, gave a good yield of benzoic acid, m. p. 121°.

The *hydrochloride* slowly crystallised from dilute hydrochloric acid (1 : 1) in broad, glistening plates, m. p. 235—242° (Found: Cl, 13·2. $C_{14}H_{18}ON_2,HCl$ requires Cl, 13·3%). The *chloroplatinate* formed orange crystals (Found: Pt, 22·6. $2C_{14}H_{18}ON_2,H_2PtCl_6$ requires Pt, 22·4%). The *picrate*, obtained as an oil which solidified slowly, crystallised from alcohol in yellow, glistening prisms which lost alcohol of crystallisation at 98° and melted to a clear liquid at 138°.

The iso*Nitroso-derivative* (III).—The sparingly soluble *hydrochloride* was obtained by adding a dilute solution of sodium nitrite to a solution of the base in dilute hydrochloric acid. After recrystallisation from very dilute alcohol it melted at 258° (decomp.) (Found:

N, 14·2. $C_{14}H_{17}O_2N_3,HCl$ requires N, 14·2%). When warmed with a little water and a slight excess of sodium bicarbonate, it gave the iso*nitroso*-compound as a bright yellow solid, which crystallised from alcohol in slender needles, m. p. 183° (decomp.) (Found: C, 65·3; H, 6·4; N, 16·15. $C_{14}H_{17}O_2N_3$ requires C, 65·0; H, 6·6; N, 16·2%).

The *dibenzoyl* derivative of (III) was readily prepared by the Schotten–Baumann method. It crystallised from alcohol in clusters of colourless needles, m. p. 148° (Found: C, 72·1; H, 5·3; N, 9·05. $C_{28}H_{25}O_4N_3$ requires C, 71·95; H, 5·35; N, 9·0%). The *diacetyl* derivative, m. p. 180—181° (decomp.), also was easily obtained by heating the base or its hydrochloride with acetic anhydride for a few minutes (Found: N, 12·4. $C_{18}H_{21}O_4N_3$ requires N, 12·35%).

The reactions of benzoylacetonitrile and of other nitriles of the type $CH_2R{\cdot}CN$ with various reactive bases are under investigation.

We wish to thank Prof. C. V. Raman, F.R.S., for giving us facilities for carrying out this work.

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[*Received, December 29th,* 1926.]

CXCI.—*Melting Points and Heats of Crystallisation of Homologous Series. Part III. Myristic Acid Derivatives.*

By W. E. Garner and J. E. Rushbrooke.

It has been shown previously (J., 1926, 2491) that the heat of crystallisation of the monobasic fatty acids above C_{10} increases by 2·060 Cal. for every two methylene groups added to the carbon chain; and also that for an even member the heat of crystallisation divided by the absolute melting point increases regularly as the series is ascended. From these two relationships the empirical equation (1) was derived for the melting points of the even members of the monobasic acids:

$$T = (-3{\cdot}61 + 1{\cdot}030n)/(-0{\cdot}0043 + 0{\cdot}002652n)\,. \quad . \quad (1)$$

where n is the number of carbon atoms in the chain.

If it be assumed that the increment in the heat of crystallisation per methylene group is the same for all homologous series above C_{10}, then an equation of a general character, (2), would be expected to be valid for all series:

$$T = (x + 1{\cdot}030n)/(y + 0{\cdot}002652n)\,. \quad . \quad . \quad . \quad (2)$$

where x and y are constants depending on the nature of the terminal groups.

In order to check the applicability of equation (2) to any particular series it is necessary to know the value for the heat of crystallisation of one of the even members of the series. In the present investigation, the data necessary for such a test have been procured in the case of the monobasic amides, alcohols, and methyl and ethyl esters. The amides, like the acids, form a series in which the melting points alternate from the odd to the even members, but the alcohols and esters are non-alternating.

The fourteenth member of each of these series was chosen for the test, and the results are in Table I. From the values of x and y in this table, the melting points (*i.e.*, the setting points or equilibrium values) of the members of five homologous series have been calculated and these are given by the continuous lines in the diagram. The experimental values of the melting points culled from numerous sources are shown in the diagram by vertical lines, the length of which indicates their range. The agreement between the calculated and the experimental melting points is within 1—2% and is as good as could be expected in view of the fact that the melting points of homologous series are not known with great accuracy, and that a small change in the constants of equation (2) produces a marked change in the calculated curve.*

TABLE I.

Substance.	Setting point, $t°$.	Q (Cal./mol.).	Q/T.	x.	y.	Heat of cryst. of terminal groups.
I. Alternating series.						
Myristic acid ...	53·7°	10·74	0·03287	−3·68	−0·00426	−1·62
Myristamide ...	103·0	12·92	0·03436	−1·50	−0·00277	+0·56
II. Non-alternating series.						
Methyl myristate	18·35	10·63	0·03647	−3·79	−0·00066	−1·73
Ethyl myristate	11·0	11·17	0·03933	−3·25	+0·00220	−1·19
Myristyl alcohol	37·7	11·76	0·03785	−2·66	+0·00072	−0·60

The melting points as determined by the ordinary method may or may not be identical with the equilibrium values for these temperatures given by the setting points. Partington and Stratton (*Phil. Mag.*, 1924, **48**, 1089) have recorded that the setting point of palmitic acid is lower than its melting point, and we also have observed the same phenomenon with palmitic and eicosoic acids. As Smits has shown ("The Theory of Allotropy," 1922), the melting point varies with the rate of heating if equilibrium between the various molecular forms in the liquid or solid states is established slowly. Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905) have

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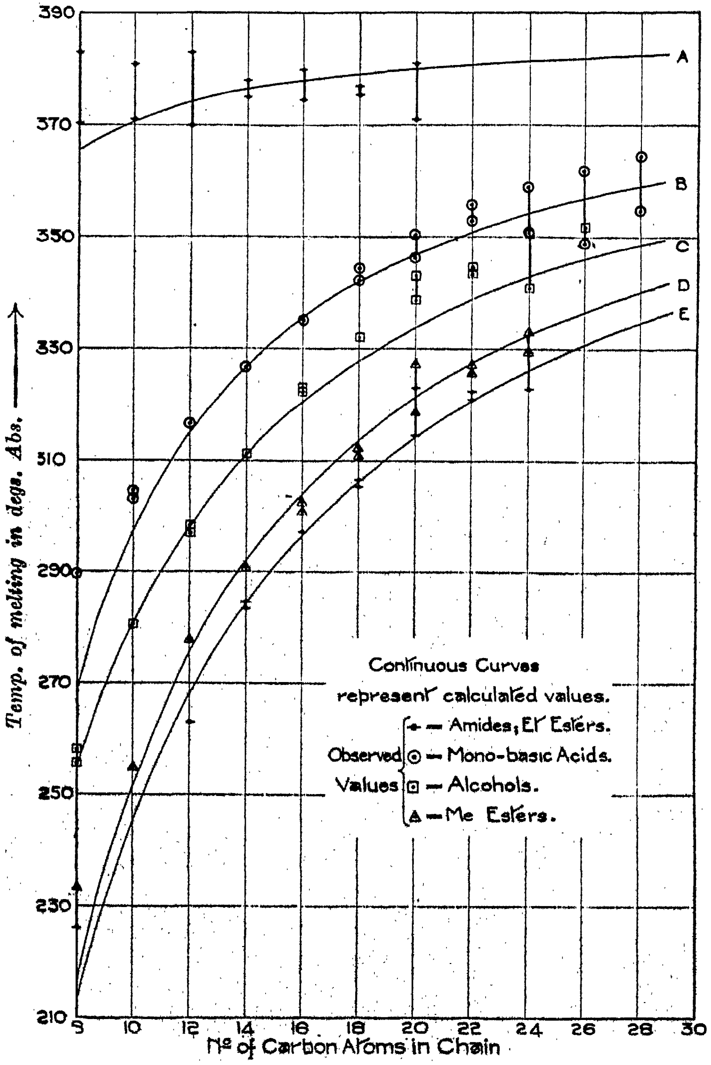
* It is desirable that the constants in equation (2) be determined more accurately by measurements of the heats of crystallisation of higher members of the monobasic acid series.

FIG. 1.



observed that the melting points of the long-chain fatty acids decrease after the solids have been kept for a long time. This points to slow changes occurring in the solid state and indicates that the phase equilibria are not established rapidly. It would therefore be expected that the melting points of these substances would vary with the rate of heating, and this would account for the wide range of the experimental values.

The melting points of the alcohols and acids recorded by Levene and Taylor and others for the 18—26th members lie on a curve which is 4—5° higher than the calculated curve. It is not unlikely that this discrepancy is due to the fact that the experimental melting points are not equilibrium values. In the case of the esters, the divergences from the theoretical curve are not large over the whole range from $n = 8$ to $n = 28$.

The agreement is of such a nature as to provide some justification for further work along these lines.

Up to the present, very few quantitative relationships, other than those of a thermodynamical character, have been discovered between the melting points of organic compounds and their other physical properties. This lack of quantitative knowledge applies not only to the melting points but also to other properties which are likewise sensitive to changes in chemical constitution. The factors determining the numerical values of constitutive properties are imperfectly understood and it is difficult to discuss even qualitatively their dependence on chemical constitution.

On account of the similarity which exists between the processes occurring at the melting point and those associated with chemical change, it is not unlikely that the application of the laws of chemical change to melting-point phenomena will yield information of importance for the study of the relationship between melting point and chemical constitution. In the previous paper (*loc. cit.*, p. 2496) a theoretical equation for the melting points of homologous series was deduced along these lines :

$$T = \frac{Q}{4{\cdot}57}\left\{\tfrac{1}{2}(n-2)\log\frac{k_1''}{k_1'} + \log\frac{k_2''}{k_2'} + \log\frac{k_3''}{k_3'} + \log n\right\} \quad . \quad (3\text{A})$$

This equation, which applies only to those homologous series in which no chemical association occurs in the liquid and solid states, contains four variables—the melting point, T, the heat of crystallisation, Q, a number of probability factors, and the number of carbon atoms in the chain, n.

This equation can be expressed in a more convenient form by adopting the conception that for each group in the molecule there is an *equilibrium constant* which determines its distribution between the solid and the liquid phase. This involves making the hypothesis that the groups forming the carbon chain can detach themselves from the surface of the crystal or rejoin the surface independently of their neighbours. This is rendered highly probable by the possibility of rotation of the groups about the single C—C linkings. There is, however, a limitation to this freedom of movement of individual groups; any group situated between two others, which are themselves attached to the surface, is incapable of movement. Thus the equilibrium constant refers only to those groups which are in such a position that they can move away from or attach themselves to the surface. Of these groups, some will be in the liquid and some in the solid phase. The ratio of those in the solid to those in the liquid phase, or the equilibrium constant, κ, is given by $\kappa = (k''/k')e^{+Q/RT}$, where Q is the heat of crystallisation of the group in question, T is the absolute temperature, and k'' and k' are the probability factors discussed previously (*loc. cit.*). The equilibrium constant of any group will vary with temperature in an analogous manner to the equilibrium constant of chemical change.

According to this view the melting points for long-chain compounds will be given by

$$T = \log_e [\kappa_1{}^{\frac{1}{2}(n-2)} . \kappa_2 . \kappa_3 . n] \quad . \quad . \quad . \quad . \qquad (3\text{B})$$

where κ_1, κ_2, and κ_3 are the equilibrium constants of the methylene group and of the two terminal groups respectively. The value of κ_1 is readily evaluated as follows: For a carbon chain of infinite length, the melting point is 118°; at this temperature, $\kappa_1 = (k_1''/k_1')e^{+Q_1/RT}$, since the probability of attachment of a methylene group at the melting point is equal to the probability of its detachment. The equilibrium constant at any other temperature can readily be calculated from the above equation.

The values of the equilibrium constants of the terminal groups are not yet known, but there is no great difficulty in the way of their determination. A study of the heats of crystallisation of the hydrocarbons and the dibasic acids, together with the data already known, should give these directly.

The application of equation (3B) to the compounds given in Table I is complicated by the fact that the acids are chemically associated to double molecules in the solid and liquid states, whereas the esters occur as single molecules in the solid state (compare Müller and Shearer, J., 1923, **123**, 2043, 3152, 3156). The amides have not yet been investigated by *X*-ray methods, but on account of the similarities between the $-CO_2H$ and $-CO{\cdot}NH_2$ groups and also since the amides and acids give alternating series, it will be assumed that the amides, like the acids, are chemically associated in the solid and liquid states. It is necessary to discuss the alternating and non-alternating series separately.

Alternating Series.—The melting points of alternating series will be given by a modified form of equation (3A). The molecules are practically twice the length of corresponding members of the non-alternating series, the heat of crystallisation per g.-mol. is doubled, and log n in equation (3A) is replaced by $\frac{1}{2}\log 2n$ in (4A):

$$T = \frac{Q}{4{\cdot}57}\left\{\tfrac{1}{2}(n-2)\log\frac{k_1''}{k_1'} + \log\frac{k_2''}{k_2'} + \log\frac{k_3''}{k_3'} + \tfrac{1}{2}\log 2n\right\} \quad (4\text{A})$$

and

$$T = \log_e\left[\kappa_1^{\frac{1}{2}(n-2)} . \kappa_2 . \kappa_3 . (2n)^{\frac{1}{2}}\right] \quad . \quad . \quad . \quad . \quad (4\text{B})$$

When $n = 14$, the numerical value for the terms in the brackets is 7·18 (for myristic acid). If we replace $\frac{1}{2}\log 2n$ by $\log n$, the value increases to 7·60. This change alone would lower T by 18°. Thus association has by no means an insignificant effect on the melting points of homologous series.

If our assumptions be correct, the amide will differ from the acid only in the value of the equilibrium constants of the chemically associated groups $(\text{-CO}{\cdot}\text{NH}_2)_2$ and $(\text{-CO}_2\text{H})_2$. The equilibrium constants for these groups are given by $\kappa_3 = (k_3''/k_3')e^{+2Q_3/RT}$, where Q_3 is the heat of crystallisation of the terminal group. Q_3 for the amide is 2·18 Cal. greater than for the acid, and this difference will affect κ_3 very materially and through it the melting point; k_3''/k_3' may be different for the two substances, but the values of this ratio are unknown.

It is clear, however, that the main factor which is responsible for the amide melting 50° higher than the acid is the high heat of crystallisation of the $(\text{-CO}{\cdot}\text{NH}_2)_2$ group. In (4A), if we assume that the terms in the brackets are the same for the amide and the acid, then Q/T = constant. Q/T for the amide is 0·03436, and for the acid 0·03287, and these values are sufficiently in agreement to warrant the above conclusion.

Non-alternating Series.—The ethyl ester possesses one more point of attachment in the crystal than the methyl ester. This is due to the additional methylene group in the alkyl chain. The equilibrium constant for this group, κ_4, is equal to $(k_4''/k_4')e^{+Q_4/RT}$, where Q_4 is its heat of crystallisation. $Q_4 = 0{\cdot}54$ instead of the normal value 1·03 Cal. found for the acid chain. The equilibrium constant, κ_4, is lower than κ_1 for the groups of the acid chain, or, in other words, the tendency for the methylene group in the alkyl chain to enter the solid state is much lower than for the same group in the acid chain. Thus the low melting point of the ethyl esters, when compared with the methyl esters, can be ascribed to the low heat of crystallisation of the methylene group in the alkyl chain.

EXPERIMENTAL.

The esters of myristic acid and myristyl alcohol were obtained from Eastman Kodak Co., and were purified by distillation or crystallisation until a constant setting point was obtained. Myristamide was prepared from a pure specimen of myristic acid and purified by crystallisation.

The details of the experimental technique were as described previously. The calorimeter had a water equivalent of 345·3 cal./deg.

The experimental data are recorded in Tables II—V. The heats of crystallisation of myristamide and myristyl alcohol are probably correct to within 0·5% and those of the esters to within 1%.

TABLE II.

Myristamide : setting point, 103·5°.

(Weight of substance, 6·5294 g.; glass, 3·8847 g.; platinum, 0·2008 g.; nickel, 3·3121 g.)

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1— 4	64—15°	50·73°	0·586°	11—12	110—15°	95·75°	2·273°
5— 7	100—15	84·75	1·045	13—14	127—15	112·68	2·545
8—10	110—15	95·56	2·278	14—17	139—15	123·94	2·725

I. From 1—7, σ_S = 0·535 cal./deg.

II. From I and 8—17, σ_L = 0·640 cal./deg.; Q = 56·84 cals./g.

A large number of measurements were made over the temperature range 110—139° in order to make quite sure that the high value for σ_L given above was correct. The amide when fused had a pale yellow colour which could not be removed by repeated crystallisation.

TABLE III.

Myristyl alcohol : setting point, 37·7°.

(Weight of substance, 10·9602 g.; glass, 6·1894 g.; platinum, 0·2008 g.; nickel, 3·9133 g.)

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1—3	1—18°	−17·13°	−0·297°	9	34—18°	+15·97°	+0·333°
4	24—18	+ 6·36	+0·119	10—12	39—18	21·23	2·146
5	26—18	8·31	0·156	13	56—18	37·48	2·538
6	28—18	10·09	0·194	14—15	60—18	42·43	2·643
7	30—18	12·08	0·233	16—18	66—18	47·73	2·785
8	32—18	14·01	0·279	19	75—18	57·35	3·032

I. From 1—9, σ_S = 0·432 cal./deg.

II. From I and 10—19, σ_L = 0·612 cal./deg.; Q = 54·86 cal./g.

Myristyl alcohol occurs in two solid modifications, one of which is unstable between 0° and 34°. The above value of Q refers to the modification stable at room temperature.

TABLE IV.

Methyl myristate : setting point, 18·35°.

(Weight of substance, 10·9144 g.; glass, 6·1791 g.; platinum, 0·2008 g.; nickel, 3·0904 g.)

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1—3	1—13°	−12·25°	−0·232°	6— 8	20—13°	6·96°	1·526°
4	3—13	− 9·92	−0·190	9—11	50—13	36·93	2·155
5	6—13	− 6·95	−0·135				

I. From 1—5, $\sigma_S = 0·475$ cal./deg.
II. From I and 6—11, $\sigma_L = 0·526$ cal./deg.; $Q = 43·90$ cal./g.

In experiments 6—11, the ester took 60 minutes before crystallisation was complete, as compared with 20—25 minutes for the amide and alcohol. On account of the long middle period, a radiation correction of approx. 0·04° was sometimes applied. This makes the above value of Q less accurate than those of the amide and the alcohol, but the error is not greater than 1%.

TABLE V.

Ethyl myristate : setting point, 11·0°.

[Weight of substance, 11·0523 g.; glass, 4·6576 g.; platinum 0·2008 g.; nickel (except Expts. 6—8), 2·034 g.; nickel (Expts. 6—8), 2·1498 g.]

Expt. No.	Temp. range.	Fall in temp.	Rise in temp.	Expt. No.	Temp. range.	Fall in temp.	Rise in temp.
1	0—15°	−14·58°	−1·678°	6— 8	45—15°	30·09°	0·579°
2	3—15	−11·99	−1·619	9—11	−9—15	−23·99	−1·842
3—5	6—15	−9·32	−1·500				

I. From 6—8, $\sigma_L = 0·500$ cal./deg.
II. From I, 1—5, and 9—11, $\sigma_S = 0·498$ cal./deg.; $Q = 43·6$ cal./g.

Sixty minutes elapsed before the melting of the ester was complete.

Summary.

The heats of crystallisation of a number of derivatives of myristic acid have been determined, and the results have been employed in the calculation of the melting points of certain homologous series, *viz.*, the amides, methyl and ethyl esters of the monobasic fatty acids, and the monohydric alcohols. The calculated melting points are in good agreement with the experimental values.

The effect of the chemical constitution of the polar terminal group on the melting point has been discussed from the standpoint of the theory of melting points put forward previously. The heat of crystallisation of the terminal group is shown to play a dominant part in determining the *equilibrium constant* of the group and, through it, the melting point.

THE RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON.
[*Received, May 5th, 1927.*]

FARADAY LECTURE

(Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution on May 18th, 1927.)

Problems and Methods in Enzyme Research.

By RICHARD WILLSTÄTTER.

NEARLY sixty years have elapsed since the death of Faraday. I count it a unique distinction that I may to-day address the Chemical Society in memory of this great pioneer, in the room so closely associated with his labours. I am conscious that it is a special honour to be allowed to join that small band of scientists from various lands—there have so far been twelve—who have spoken in remembrance of Faraday. In these memorial lectures the history of science is reflected, which, in the image of Goethe, may be compared to a great fugue in which the voices of the nations are heard in succession. My reverence for the genius to whom we pay homage is coupled with veneration for the memory of the many other great investigators whom your country has produced. The presence of so many distinguished colleagues in this room augments my sense of the importance of the present occasion, but my thoughts nevertheless travel beyond the living, to the immortals.

My predecessors have mostly selected single chapters of Faraday's lifework as a starting point for a discourse on experimental contributions or theoretical discussions in the realms of physics and chemistry. Faraday's work provides a store of stimulating suggestions, one which is neither exhausted nor likely to become so for a long time to come. Since none of my predecessors has referred to Faraday's experiments "on the power of metals and other solids to induce combination of gaseous bodies," I should like to take this early fundamental investigation on catalysis as my starting point in a discussion of organic catalysts.

This investigation was carried out in the year 1833, at the time, therefore, of E. Mitscherlich's work on the formation of ether from alcohol by contact with sulphuric acid. Faraday and Mitscherlich recognised the frequency of such reactions. Mitscherlich called them reactions through contact, and compared ether formation to the decomposition of hydrogen peroxide, the alcoholic fermentation of sugars, the formation of acetic acid from alcohol, and the decomposition of urea ("Für sich erleiden diese Substanzen keine Veränderung, aber durch den Zusatz einer sehr geringen Menge Ferment, welches dabei die Kontaktsubstanz ist, und bei einer bestimmten Temperatur, findet diese sogleich statt." . . . By themselves these substances do not undergo any change, but they decompose at once at a given temperature on addition of a very small quantity of a ferment which is the contact substance).

These investigations were discussed by Berzelius in his 15th annual report on the progress of the physical sciences. He collected a number of known cases of inorganic and organic contact actions, and grouped them for the first time under the definition of "Catalysis." Although he saw in catalysis "a new force causing chemical action, present both in organised and in unorganised nature," he was far from rejecting the idea "that it should be considered an action independent of the electro-chemical relationships of matter."

The inorganic contact substances had, in connexion with the earliest observations on catalysis, already been compared with natural ferments, and when, towards the end of the century, W. Ostwald gave new life to research by his definition of catalysis, his suggestion of kinetic measurements led to the stimulation of enzyme research by the methods of physical chemistry. The parallelism between enzymes and artificial inorganic catalysts was particularly emphasised by G. Bredig through his experiments with inorganic ferments, which revealed a manifold and far-reaching agreement between the two kinds of catalysts. Conversely, observations on the behaviour and the nature of enzymes promise new knowledge of the general theory of catalysis. My own experiments and those of my pupils, of which it is my privilege to speak to-day, deal with the adsorption relationships and some other properties of enzymes, more particularly their specificity. With the great example of Faraday before me, I venture to bring forward these modest contributions, encouraged by the deep interest which Faraday evinced in the nature of the relationship between catalyst and substrate. The expectation does not appear altogether unjustified that some new results with enzymes, pointing as they do to a close relationship between the phenomena of adsorption determined by affinity and those of catalytic action, may contribute to a more general knowledge of the selective action of chemical adsorption and of the specificity of catalysts. In their strict specificity, and also in their great potency within a narrow range of reaction conditions, the enzymes are superior to the long-known inorganic contact substances. The modern development of catalysis in chemical industry has emphasised the importance of the problem of improving inorganic catalysts on the pattern of the enzymes so as to make them more selective and at the same time more active. Moreover the activation of enzymes is being imitated with much success. These phenomena of activation and also those of catalyst poisoning, being susceptible of quantitative measurement, have of late led to remarkable information concerning the nature of catalysts, for example, in the researches of C. N. Hinshelwood, W. G. Palmer, F. H. Constable, and H. S. Taylor.

Faraday examined the action of platinum on a mixture of hydrogen and oxygen. He rejected the idea that a contact substance enters into a chemical union. It is, however, not quite correct, as has often been done, to quote his explanation of the process as being a purely physical one. Faraday spoke of "that attractive force, possessed by many bodies in an eminent degree, and probably belonging to all, by which they are drawn into association more or less close, without at the same time undergoing chemical combination . . . and which occasionally leads, under very favourable circumstances . . . to the combination of bodies simultaneously subjected to this attraction. I am prepared myself to admit . . . both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance."

In Faraday's view, catalysis and adsorption are related. As unequivocal examples show nowadays, many adsorption phenomena depend on chemical affinity and more especially on the residual affinity of the molecules. The attempt to explain adsorption by means of capillarity breaks down in the case of selective adsorption, as observations on the selective behaviour of adsorbents towards enzymes show.

The behaviour of hydrogen and oxygen towards platinum has ever remained an important problem since the above-mentioned fundamental investigation by Faraday. As I was able to show a few years ago, in conjunction with E. Waldschmidt-Leitz, platinum is capable of transferring hydrogen catalytically only in the continued presence of oxygen. There are various views with regard to this rôle of oxygen in hydrogenation catalysis. Whilst, on the one hand, M. Bodenstein considers the oxygen merely of importance for the renovation, that is, the detoxication, of the platinum surface, R. Kuhn, on the other hand, has developed the view that the oxygen poisons the platinum to some extent, and that without its co-operation only recombined hydrogen molecules would encounter the substrate on the platinum surface. This view makes the oxygen content responsible for the variety of the recombination stages of the hydrogen at the platinum surface. It should, however, be borne in mind that even the course of the reaction in hydrogenation, for instance of naphthalene (according to R. Willstätter and F. Seitz), may vary according to the extent to which the platinum is charged with oxygen. I consider it, therefore, more probable that the affinity fields of the platinum are so changed by the taking up of oxygen that a new contact substance results, specifically adapted to the hydrogenation. The greater or smaller extent of the oxygen charge would then produce definite peculiarities in the affinity. Platinum charged with oxygen must be ranged among the mixed catalysts, and may be compared with the enzyme–activator complexes. To my mind the experiments indicate that, according to the nature of the contact substance, the naphthalene is variously activated and thereupon hydrogenated to the different stages that are observed. The existence of some relationship between the contact substance and the naphthalene may be inferred from the fact that with platinum *cis*-decahydronaphthalene is exclusively produced; with nickel, on the other hand, the *trans*-isomeride is the chief product of the hydrogenation.

Berzelius relinquished any attempt to explain the processes of catalysis, and emphasised in his discussions with Liebig the danger of explaining incompletely understood phenomena by means of hypothetical assumptions. To-day this reserve is still maintained and approved by many; the absence of an explanation, however, has limited the interest in the phenomena. There is no single method of scientific investigation which can be described as the right one in all circumstances. A hypothesis may vary in value according to the mentality and the temperament of the investigator and according to its utility in suggesting and co-ordinating new observations. A hypothetical explanation of incompletely understood phenomena is often a necessary condition of scientific progress.

An elaboration of an incomplete attempt at explanation by Liebig may perhaps be seen in the hypothesis of C. Nägeli (1879), who explained ferment reactions by the transference to the substrates of "states of motion," that is, of "vibrations of the atoms and particularly of atomic groups." His view seems to me to have been improved by J. Böeseken and to have been further developed, in accordance with modern conceptions, by the consideration of electron orbits instead of atomic vibrations.

The definition of W. Ostwald (1894), which gave a fresh stimulus to research, is as follows: "Katalyse ist die Beschleunigung eines langsam verlaufenden chemischen Vorgangs durch die Gegenwart eines fremden Stoffes" (Catalysis is the acceleration of a slow chemical process brought about by the presence of a foreign substance). Ostwald considered the principle that the catalyst changes the reaction velocity only, to be the key to the interpretation of catalytic phenomena. As he himself stated, the new point of view which was of most value to research was the conception that a catalyst or enzyme cannot bring about a reaction which does not occur without its co-operation. This conception still holds the field, although it is true that several investigators (J. J. Thomson, H. E. Armstrong) did not agree with it. This principle, which has been deduced from thermodynamical considerations, should not, however, be maintained too dogmatically. At the present day it seems to me to have little value and to hamper progress. Like a dogma, it hinders us in any attempt to find a new explanation of the phenomena of catalysis without intermediate compounds and of the causation of reaction without an influx of energy.

The catalyst may function in degrees of association with the substrate, varying from *fixation* to *approach*. It can, naturally without extraneous energy, bring about a change of constitution in the substrate molecule, and it is only through this constitutional change that reaction may be induced. Here it is not an essential, nor even a general condition, that the molecule should change to a new compound capable of independent existence, as, for instance, to an isomeride such as the so-called γ-glucose (with a changed oxygen bridge) which has been postulated as an intermediate in the action of F. G. Banting and C. H. Best's insulin on glucose. In general the catalyst only requires to bring about a change in the molecule such as was first suggested intuitively by F. Raschig (1906), in advance of exact interpretation. F. Haber (1922) considers the heterogeneous catalysis of gas reactions to be a process "in which the first phase . . . is apparently represented by an electrodynamic distortion of the molecules by the atomic fields at the interface between the solid contact substance and the gas." M. Bodenstein also bases an explanation of the activation of hydrogen by platinum on the deformation of the molecules.

Our new views concerning the structure of atoms and molecules permit us to characterise the hypothesis of the deformation of molecules somewhat more fully as the deformation of their electron orbits. Making ourselves more independent of the hypothetical formulation of discrete orbits, we may, in accordance with E. Schrödinger's wave mechanics, conceive the action of the catalyst on the substrate, through fixation or approach, to be such that the continuous distributions of the electrical charges of the catalyst and the substrate mutually influence each other. A superposition of the fields of charge associated with catalyst and substrate may amount to the same thing as the presence of points of greater condensation of the charge.

The immense store of facts comprehended in "catalysis" contains examples of so diverse a nature that it would be futile to attempt to explain all the phenomena by means of a single hypothesis. The Ostwald school has proved the existence of intermediate reactions in important cases. The explanation is derived from A. de la Rive's assumption (1846) of a platinum–oxygen compound and from the much older investigation by N. Clément and Ch. B. Désormes of the action of oxides of nitrogen on sulphurous acid. In the case of homogeneous systems this explanation has proved so fruitful that E. Abel declared: "nicht Stoffe, nur Reaktionen katalysieren" (Only reactions may catalyse, substances do not). It is a weakness in Böeseken's views that they do not contemplate this kind of catalytic reaction. Although many catalytic phenomena may be explained without postulating the formation of stoicheiometrically constituted intermediate products, and although a theory of affinity modification without the production of intermediate stable compounds has its uses, such a theory can nevertheless not lay claim to universal validity. In enzyme chemistry there is no theory which appears to be so fruitful and so satisfactory as that assuming the existence of intermediate compounds between catalyst and substrate. Accordingly this is the specifically chemical conception of the primary process of enzyme action, in contradistinction to the physical one, the colloidal–chemical adsorption process suggested by W. M. Bayliss, G. S. Hedin, and J. M. Nelson.

According to Böeseken a catalyst produces a very rapid change ("dislocation") of the links which it activates by means of a "temporary, very unstable addition to the specific links of the molecules" ("action orientatrice"), and then, without forming a true compound, transfers peculiarities of its own "open system" by induction to the closed system of the substrate ("action dislocante"). By way of explanation it is represented that the catalyst changes the electron orbits of the substrate. According to N. Bohr's view this deformation of an electron orbit would occur through the action of a force, and would therefore involve a change in the energy of the electron. The assumption of an energy change might be avoided in the case of the superposition of two continuous fields of charge. Thus no change in the energy level or in the distributions of charges would occur.

One of the most general questions on the subject of catalysis is concerned with the chemical nature of the catalysts. The point has hitherto been somewhat neglected, but the above-mentioned observation on hydrogenation catalysis by platinum suggests that our knowledge of the chemical composition, even of simple inorganic catalysts, is still very incomplete. There are many non-specific catalytic actions, especially cases of hydrolysis which are catalysed by acids and alkalis. Thus the non-specific catalytic activity of hydrogen ions may bring about the fission of proteins and their degradation products, of carbohydrates, whether composed of many or only a few monose-units, and of the fats and other esters. The need for selective and highly active inorganic catalysts has in the last seventeen years led to remarkable results in directing the course of reactions by means of mixed catalysts. These results, possessing great practical value as well as theoretical interest, are largely due to the investigations of A. Mittasch and others in the laboratory of the Badische Anilin- und Soda-Fabrik.

A fundamental conclusion reached by Mittasch is "that the catalytic action of iron becomes both more intense and more permanent on the admixture of numerous metals and oxides." In the catalytic oxidation of ammonia, ferric oxide to which bismuth oxide has been added gives, according to Mittasch, quite as good results as an efficient platinum catalyst. Yet another example among many : pure zinc oxide acts on a mixture of carbon monoxide and hydrogen under pressure in the direction of methanol formation; if a small quantity of iron is added, the reaction is diverted towards the formation of hydrocarbons. The oxidation of carbon monoxide by means of air at the ordinary temperature was made possible by the use of certain mixtures of the oxides of the heavy metals, for example, those of manganese, copper, cobalt, and silver (hopcalite), in the experiments of A. B. Lamb, W. C. Bray, and J. W. C. Frazer. These mixed catalysts have close analogues among the enzyme systems; trypsin differs from trypsinkinase, and papain from papain–hydrogen cyanide, not only in potency, but also in specificity.

It is not enough to assume that the admixture to the simple catalysts merely increases the frequency with which the catalytically active atoms project from the lattice. This effect is produced by only a small category of added substances, the carriers. It is rather that catalysts composed of two or more substances are so clearly characterised by specific actions, or deflection of the reaction, that the status of new substances must be ascribed to them. Hitherto it has been generally accepted as a principle in chemistry that the chemical properties of the constituents are lost in compounds, but are preserved in mixtures. This principle has ceased to be valid since more delicate chemical means have become available for the detection and measurement of chemical affinities. Observations on platinum containing oxygen, on the activated catalysts or mixed catalysts of Mittasch and his co-workers, as well as on activated enzymes, have convinced me of the validity of the statement that *mixtures may have the nature of new chemical compounds*. The similarity between mixtures and compounds may be explained by considering that the electrostatic and the electromagnetic fields of force of the individual components of an intimate mixture may exert a mutual influence on each other. Thus a new kind of affinity field would result. The same explanation as that already brought forward for the action of a catalyst on the substrate, be it a deformation of electron orbits or a superposition of fields of charge, may be adduced. Thus it becomes intelligible that, by mixing two or more components, individual catalysts may result having an enzyme-like specificity and potency comparable with that of homogeneous compounds; whereas the comparatively simply constituted fields of affinity of the elementary atoms do not suffice for this purpose. The very narrowest range of specificity is a peculiar property of the organic catalysts of high molecular weight produced by the living cell. There appears to be a deep gulf between the inorganic catalysts and the enzymes, the chemical constitution of which is still quite obscure. In reality this gulf has already been bridged by accurately defined organic compounds which act like enzymes.

Chlorophyll may be considered one of the organic catalysts; I have refrained from calling it an enzyme, as this would have been a mere empty phrase. It is now, however, becoming useful to recognise connecting links between enzymes on the one hand and catalysts, accurately defined chemically, on the other. Colloidal chlorophyll forms a dissociating additive complex with carbon dioxide. In conjunction with A. Stoll I have suggested as an explanation of photosynthesis that the adsorbed radiation produces a molecular rearrangement of the carbon dioxide. An isomeric peroxide form of the latter would then decompose into oxygen and hydrated carbon.

Similarly oxyhæmoglobin partakes of the nature of enzymes. Recently I have shown, in conjunction with A. Pollinger, that the oxyhæmoglobins of various animal species act exactly like peroxydases of an unequal potency. Under similar conditions 1 mg. of the oxyhæmoglobin from horse blood, ox blood, and pig's blood furnishes respectively 0·152, 0·114, and 0·093 mg. of purpurogallin in the oxidation of pyrogallol. The oxyhæmoglobins do indeed correspond to peroxidative enzymes of low potency, as they are about 10,000—30,000 times weaker than our best preparations of vegetable peroxydases. We attribute the difference in potency of the individual hæmoglobins to the fact that the same specifically active (prosthetic) group is influenced in its action by association with the globin molecules, which in the various varieties of blood differ in their constitution. The peroxidative reaction of the iron-containing pigment group which is united to various globin complexes is therefore subject to modification, so that the hydrogen peroxide adsorbed by the individual oxyhæmoglobins is activated in a varying degree.

Hence differences in the constitution of the colloidal carrier of the active group result in differences in the potency of this group. This may show how the differentiation of the enzymes, the so-called species specificity, may be determined by variations in the colloidal complex.

The dependence of catalytic activity on chemical constitution has recently been further investigated in the Munich laboratory by R. Kuhn and L. Brann in quantitative experiments with hæmochrome; they used as examples enzyme-like catalysts with accurately defined differences in their chemical constitution. If hæmoglobin is broken down to hæmin, the peroxydase action is enfeebled and the new form of organically bound iron shows a considerable catalase activity which was previously lacking. According to a letter from Prof. R. Kuhn, the activity of hæmin, functioning as catalase, may, under the best conditions, be related to that of G. Bredig's colloidal platinum as 1 : 1·5, and to that of the best preparations of liver catalase, purified by S. Hennichs's adsorption process, as 1 : 1000. In mesohæmin, which is richer by two atoms of hydrogen, the dependence on the p_H of the peroxidative action is considerably changed (optimum 6·5, instead of 5) and the catalase action is lacking. We see, therefore, that the catalytic action is subject to considerable variation without change in the iron content and without the possibility of attributing the variation to changes in the degree of dispersion.

Gradations in colloidal dispersion cannot provide an explanation of the highly selective and specific affinities of enzymes. A few years ago it still seemed doubtful whether enzymic actions depend on peculiar conditions in the dispersion of any known substances, or whether they depend on definite organic compounds of unknown constitution. Our views on this fundamental question have been clarified more especially by the three following sets of observations:

(1) In some cases chemical analysis had caused enzyme action to be ascribed to known organic substances or types. The enzymes which had served for the analyses were, however, very impure; they contained only a few units per cent. or even a fraction of a unit per cent. of the purified enzymes available to-day. According to A. Fodor, the saccharase of yeast was supposed to be substantially identical with a carbohydrate yeast-gum, but now the enzyme has been wholly freed from yeast-gum without change of activity. More frequently and with more reason relationships have been assumed between enzymes and proteins. Thus E. Fischer, in his Faraday lecture, deduced from observations then available, indeed with a certain degree of probability, that the enzymes "are derived from proteins and possess a protein-like character." In a variety of cases it has, however, been possible to purify enzymes to

such an extent that the protein reactions disappear completely (lipase, peroxydase, saccharase).

(2) It results from recent observations by H. Kraut and myself that simple inorganic colloids, showing peculiarities which were likewise thought to be attributable to dispersion, actually owe their specific properties to the individual chemical structure of their molecules. The gels of alumina, ferric oxide, stannic acid, etc., do not consist of metallic oxides with various quantities of adsorbed water, but there are numerous metallic hydroxides with various amounts of water in chemical combination.

(3) In making pure preparations of enzymes from the living cell, they are subjected to great changes in dispersion in the passage from the cells into solution, then into adsorbates, and again into solution; mixtures of enzymes could be separated into their components. Yet in many such cases the enzymic action was preserved almost quantitatively.

The conception of the enzymes as peculiar organic compounds suggests the problem of isolating them in a state of purity. The task of increasing the concentration of the enzymes has progressed so far that they may be more accurately characterised. For we can now distinguish between the properties of the enzymes themselves and the influence of accompanying substances, some of which form with the enzymes naturally occurring, physiological complexes, whilst others become accidentally associated with them during the isolation from the cells. In order to increase the concentrations of the enzymes, which are very low *in situ* or in the crude extracts, it is essential to measure each step in the isolation and purification so far as may be possible by quantitative estimations of the relative activities of the preparations. The literature of the simplest inorganic contact substances seems as yet to be poor in such observations. When, for instance, a metallic catalyst is obtained by reduction of its oxide, it is customary to be satisfied with the conversion of an unknown small fraction of the atoms of the crystal structure into the condition in which they are available for catalysis; that is, into a condition of high energy, of smallest saturation by the other atoms of the crystal lattice. The ratio between the catalytically active atoms and the total number in the case of iron catalysts was determined last year by J. A. Almquist in experiments on poisoning by oxygen. The preparation of an inorganic catalyst should aim at increasing the efficiency of unit weight as far as possible. In the isolation of an enzyme we aim at diminishing as far as possible the mass of catalyst necessary for a given action under definite conditions.

The very labile and very soluble enzymes must be separated from many times their weight of accompanying substances such as proteins, carbohydrates, and salts, to which they are apparently united by adsorption, and this separation must be effected without the use of the ordinary chemical means, such as conversion into salts or other derivatives. The general method which has been adopted in the investigations of recent years consists in the application of the processes of adsorption by so-called surface-active substances, such as alumina, kaolin, lead phosphate, tristearin, etc. Adsorption is made so selective that not only are the enzymes largely freed from foreign admixtures, but many are also separated from the accessory substances or activators, with which they form complexes.

The application of adsorption processes to the purification of enzymes goes back far into the past. It does not, however, seem to have been well known, or it has been considered doubtful or improbable, that the enzyme could actually be freed from the adsorbates by a process of elution. The small amount of active affinity by which the enzymes are bound in the adsorbates may in general be overcome by very gentle chemical means, for example, by very dilute solutions of alkalis or alkaline phosphates. In this case we do indeed often observe, for instance with lipase, that the elution of an enzyme which takes place quite easily and in good yield in the early adsorption processes becomes more and more difficult as purification proceeds, giving smaller and smaller yields until finally these means fail to decompose the adsorbates. At lower degrees of purity the adsorbents generally also bind certain substances which accompany the enzymes as adsorption complexes; these substances are able to co-operate in bringing about elution as well as adsorption, and sometimes this is the only mechanism for effecting these processes (co-adsorbents and co-eluents).

The oldest reference to the adsorption of enzymes which I have been able to find is the isolation of pepsin by A. Vogel (Munich, 1842). Pepsin was precipitated together with proteins by means of lead acetate, and again passed into solution when the precipitate was treated with hydrogen sulphide. One of the oldest references of this kind is the investigation by E. Brücke (1861), who was able to bind pepsin " mechanically to small solid bodies " such as calcium phosphate, sulphur, or cholesterol and to free it again from the adsorbates. Even in those days, particularly in the following year, A. Danilewsky and J. Cohnheim attempted in Kühne's laboratory to separate enzymes, more particularly the components of the pancreatic mixture, by means of adsorption processes. Differentiation of this kind was met with much later by S. G. Hedin, who found that two proteases present in the spleen behaved differently during adsorption by kieselguhr.

The adsorptive method, which had almost fallen into oblivion, was revived some twenty years ago in an investigation of L. Michaelis and M. Ehrenreich. In using adsorbents of such a kind that they have under all conditions a definitely electropositive or electronegative charge, it appeared as if the opposite charge on the enzymes, whether basic or acid in nature, determined their adsorption. Thus saccharase was believed to be an acid and trypsin to be amphoteric. It has been found, however, that these results are not valid for the enzymes themselves, but only for arbitrary aggregates of foreign substances which happen to be present in the impure solutions. Thus saccharase, which was not supposed to be adsorbed by electronegative kaolin, is readily adsorbed by this substance after the first few stages of purification, or even at once from autolysates of yeast prepared by an improved method. In many cases the true adsorption behaviour of an enzyme only appears clearly in the course of its purification. Pancreatic amylase, for example, may be adsorbed by alumina under certain conditions, as long as it is in the crude state. The purification of the enzyme can be effected by preliminary adsorption, that is, by removal of a portion through fractional adsorption, but its behaviour then changes so that it is no longer appreciably adsorbed under any conditions by alumina gels of excellent adsorptive power. The adsorption of enzymes is determined by chemical peculiarities which cannot be predicted.

Whilst amylase escapes adsorption, peroxydase provides a case of an enzyme being adsorbed not, indeed, from aqueous solution, but from one containing alcohol. The acidity of the solution commonly has an influence on the adsorption. Papain is very weakly adsorbed from an acid solution, better from a neutral one, still better from a weakly alkaline one, and in this case also much more readily from a solution containing alcohol; it is eluted from the adsorbent by weak acid. Experiments show that these adsorption processes are not at all governed by the capillarity of the substances whose surfaces are strongly developed, nor is adsorption in any way determined by such gross differences as the acid and basic nature of the enzyme and of the adsorbents. Among the various aluminium hydroxides the meta-compound (AlO_2H), which does not appreciably react either with concentrated hydrochloric acid or with sodium hydroxide, is distinguished by the most selective adsorptive action.

The success of the preparative application depends on whether it is possible to make the adsorption sufficiently selective. The smaller the quantity of adsorbent which is required, the higher is in general the degree of purity in the adsorbate. It was therefore necessary to follow the adsorption by quantitative measurements which determined the number of enzyme units taken up by 1 gram of an active adsorbent (adsorption value). In our first investigation of saccharase we obtained an adsorption value of 0·15 for alumina by improving the autolysates of yeast, by preparing suitable kinds of alumina, and by the choice of conditions favourable to adsorption. Later this value was increased twelve-hundred fold, to 200, by the proteolytic degradation of substances accompanying the enzymes, by using suitable conditions of dilution and acidity, by repetition and by fractionation. Thus the enzyme from 14 kilos. of fresh brewers' yeast was adsorbed by 1 gram of aluminium oxide and the adsorbate weighed 2·5 grams.

A more accurate insight into the course of adsorption is furnished by the adsorption isotherm according to H. Freundlich, which expresses the relationship between the quantities of enzyme in the adsorbate and in the residual solution. Since in the case under review we are not concerned with homogeneous substances, but with complicated mixtures, the adsorbed quantities depend very greatly on the initial concentrations. In the case of saccharase the use of very dilute solutions brings about a great improvement in the selective action and in the purity of preparations. Adsorption curves also show in which direction in a given case fractionation should be applied, whether the degree of purity will be improved by removal of the first or of the last fraction. Thus fractionations were controlled by the quantitative studies of H. Kraut on the adsorption behaviour of mixtures. The object was to obtain normal adsorption isotherms such as are given by homogeneous substances, and this has been attained in the case of certain enzyme preparations (saccharase). Once this is attained, the same adsorption process does not, of course, bring about any further improvement. Yet the preparations so obtained were found to be far from homogeneous. The observed adsorption curves are not those of the enzymes themselves, but of enzyme-containing complexes. The adsorption method reaches a limit of utility with certain aggregates in which the enzymes and substances most nearly related to them are firmly joined by adsorption to accompanying substances of different kinds. The proof that the constantly adsorbed enzymes are only apparently single substances follows from qualitative and quantitative analysis. If a given constituent can be tested for by colour reactions or by precipitation, it must be possible either to accumulate it or to get rid of it completely. For instance, my first investigation (with A. Stoll) on vegetable peroxydase led to preparations of which sugar groups formed a considerable part. They showed an important iron content (0·5%) which seemed to be approximately proportional to the peroxidative action. Starting from this condition, the degree of purity could be raised about fivefold by adsorption methods : meanwhile the carbohydrate constituents were eliminated and the iron content fell to one-seventh (0·06%). Hence iron does not enter into the constitution of this oxidative ferment. At the degree of purity ultimately attained, a new property of the enzyme appeared, which could not be recognised at an earlier stage : the enzyme had a reddish-brown colour resembling that of porphyrins.

Phosphorus seemed to be an essential constituent of saccharase, for its quantity amounted to 0·16—0·19% for saccharase of saccharase value 0·1—0·15 (H. von Euler and O. Svanberg). A fractionation was then carried out by means of adsorption on lead precipitates in such a way that the enzyme was isolated from the fractions containing least phosphorus. While the saccharase value rose to 2 and further to 5, the phosphorus content fell to 0·02 and even to 0·006%. The change in the ratio phosphorus : activity shows that this constituent is of no significance.

There is no sure method available for freeing the enzymes from the protein derivatives. However, if a certain enzyme in isolated cases could be freed quantitatively from accompanying proteins, this might be considered a sufficient demonstration that this enzyme neither is a protein nor requires protein for its activity. Nevertheless the tenacity with which proteins cling to enzymes has threatened again and again to impose the conclusion that the enzymes are of a protein character. Progress in the technique of methods of separation has been achieved mainly with yeast saccharase. Autolysates of yeast and the enzyme preparations made from them always gave the strong Millon reaction of tyrosine peptides, about as strongly as egg albumin. But the protein fission products responsible for this reaction only accompany the enzymes in the course of the proteolytic degradation to which the yeast plasma is subjected after destruction of the cell. It was therefore only necessary to carry out a cautious autolysis of the yeast at neutrality and to avoid the proteolytic processes in the isolation of the enzyme, in order to free saccharase completely from the substance giving the Millon reaction. On the other hand, the enzyme preparations which have been obtained in this gentle fashion are characterised by a striking tryptophan content which was discovered by H. von Euler and K. Josephson, who attributed to it a real importance as regards the composition and the function of saccharase. Actually it has been found impossible to free saccharase entirely from tryptophan by any systematic process of adsorption, but it was nevertheless possible in single cases. And my purest preparations of this enzyme show only about ¼ to ⅛ of the tryptophan content found in the preceding research (saccharase values 8·4, 11·9, and 9·7 with 0·12, 0·16, and

0·18 mg. of tryptophan per unit). The crude material, the autolysate of yeast, can, however, be obtained in such a way that after dialysis it contains much less of this amino-acid than was considered to be characteristic of the pure enzyme. The quantity of tryptophan for different saccharase units is 150 mg. in the case of ordinary yeast and 70 mg. in the autolysates formerly employed. By increasing the enzyme content of the yeast itself and by improvements in the autolysis, the quantity of tryptophan corresponding to one unit was lowered to 0·23 mg. in the case of an autolysate after prolonged dialysis. Saccharase could therefore be freed almost completely from various chemically recognisable substances of rather high molecular weight, such as carbohydrates, phosphorus compounds, and protein substances, and this without loss of activity, even without loss of stability.

By the adsorption processes the saccharase is concentrated 3000—4000 fold as compared with dry brewers' yeast. The enzymic concentration of the purest preparations corresponds to saccharase values of 11—12 obtained from the yeast autolysates of a saccharase value equal to $\frac{1}{150}$. After this degree of purification had been reached, it seemed desirable to increase the purity of the yeast itself and of its autolysates, and to test whether a greater increase of the enzymic concentration could thereby be achieved. It is possible to make yeast richer in enzymes. H. von Euler and also J. Meisenheimer had increased the saccharase content of yeast considerably by prolonged intensive fermentation. Their results were soon greatly improved upon by conducting the fermentation with very low concentrations of sugar so that the saccharase content was increased ten to fifteen times, while other enzymes, such as maltase, trypsin, and the members of the zymase complexes, suffered only a slight increase or none at all. The importance of this process therefore consists in increasing the ratio of the saccharase to those other enzymes from which it may be separated only with the greatest difficulty. Improvements were also made in the method of dissolving the enzyme, and in this connexion it was necessary to reach a better understanding of the processes which take place on the passage of an enzyme from the yeast cell into aqueous solution. The cell begins to give enzyme to the water only after its death. The liberation of a sucroclastic enzyme is itself an enzymic process and indeed a definite stage in the entire enzymic degradation of protoplasm. The liberation of the saccharase and of the maltase must therefore be separated as far as feasible from the whole process of yeast autolysis. It was possible to make these two enzymes pass quantitatively into aqueous solution in the course of a single day, accompanied by not more than one-tenth or even only one-twentieth of the substance of the yeast. The crude solutions attain saccharase values of about 1, and the dialysed solutions values of about 2·5; whereas a few years ago the purest known preparations corresponded approximately to the value 0·3. By means of the adsorption method the autolysates, obtained with the greatest possible precaution, now readily yield the enzyme, but not in a greater state of purity than the earlier autolysates, which were 100—375 times weaker. The enzymic concentrations are on the whole even a little lower, but the stability of the enzyme is greater. Here, indeed, the natural enzyme complexes seem to have been isolated by gentle means. In energetic autolysis, followed by a proteolytic process, the mass of these complexes becomes less and they become less stable. It seems that we must consider an enzyme to be composed of a specifically active group and a colloidal carrier. To this, other substances of high molecular weight cling in various ways. The colloidal carrier seems to vary somewhat in its nature, but to be necessary for the stability of the active group.

In the whole course of enzyme isolation the adsorption method has so far only served to separate the enzymes from substances which are not closely related to them. In every case the components that are most tenaciously retained are those substances which are most closely related to the enzyme in colloidal and chemical properties, for instance, its transformation products, which differ from it only by the absence of the active specific group. In this connexion we attribute importance to a process of fractional adsorption, that is, adsorption on a very finely divided precipitate, for instance, of lead phosphate, produced in the enzyme solution itself. The highest degree of enzymic purity yet attained has been reached by a fractional formation of such an adsorptive precipitate. By this means it has also become possible for the first time to separate an enzyme from the products of its inactivation, when a loss of activity has occurred through keeping or warming a solution; the more easily adsorbable portions contain the inactive, and the more difficultly adsorbable ones the active, fraction of the enzyme.

The most important and theoretically interesting problems of the adsorption method are presented by (1) the complexes of enzymes with their activators and their retarders, and (2) the natural mixtures of enzymes.

The pancreatic mixture of lipase, trypsin, and amylase offers the first example of the separation of enzymes by means of adsorption. Lipase is most readily adsorbed; it can be removed from the mixture by means of alumina and eluted from the adsorbate by means of weakly alkaline phosphate solution. Amylase and trypsin remain in solution. It should be borne in mind, however, that this process requires the use of a particular kind of alumina (γ-alumina). Another kind (β-alumina) readily adsorbs the trypsin as well. Pancreatic amylase is the least adsorbable, in a pure condition scarcely at all by ordinary means. For solutions which are still impure, kaolin is suitable for the complete adsorption of trypsin, leaving amylase behind. This investigation was continued by E. Waldschmidt-Leitz in my laboratory, and he succeeded in completely resolving the proteolytic systems of the pancreas and the intestine. In consequence of the detailed experiments of W. M. Bayliss and E. H. Starling, trypsin was supposed to be secreted by the gland in the form of an inactive precursor (trypsinogen) and changed into trypsin itself by a second enzyme, enterokinase, which accompanies it. Enterokinase is, however, no enzyme, but a specific activator of trypsin. This kinase may be separated from trypsin by adsorption with alumina, even after the latter has been activated. What was considered to be trypsinogen is a true enzyme which even in the absence of its kinase has a specific action on peptones, histones, and certain protamines. Activation by enterokinase increases the activity and extends it to more resistant substances such as fibrin, gelatin, casein, etc. Trypsin and the trypsin–enterokinase complexes prove to be two proteases differing in specificity and complementary to each other. The best means of separating trypsin and enterokinase depends, according to E. Waldschmidt-Leitz and K. Linderström-Lang, on the adsorption of the activator by a precipitate of casein produced in the solution; the trypsin remains behind quantitatively. Since trypsin free from its activator and also enterokinase are both obtainable in a state of purity, the enzyme and the kinase of various animals may be compared and combined. E. Waldschmidt-Leitz found that the trypsin of one species is activated by the kinases of other animals in quite unequal degrees; for instance, the trypsin of the pig is activated much more strongly by the kinase of the cat than by the corresponding kinase of the pig.

Apart from kinase, pancreatic protease consists of two components, the second being erepsin, discovered by O. Cohnheim in the intestinal mucous membrane. Of the two proteolytic enzymes, only erepsin is readily adsorbed by alumina (γ), according to E. Waldschmidt-Leitz. On repetition of the adsorption several times, the separation becomes complete. In the same way we can separate, by means of adsorption on alumina, the two proteases of yeast, but in this case the tryptic component is the more readily adsorbable. It is only when the enzymes of a mixture have been thus prepared in a homogeneous state that it is possible to determine their specificity. Erepsin does not act on the higher proteins, but exclusively on the simpler peptides—a point which was hitherto doubtful. The homogeneous proteolytic enzymes will in future research be the most suitable agents for the fractional enzymatic hydrolysis of proteins, in order to determine analytically the various stages in their degradation, and for preparative purposes.

Whilst the first-mentioned example was concerned with the three pancreatic enzymes, differing greatly in specificity and in properties, the last-mentioned applications of the method extend to similar closely related enzymes in which only small differences in adsorptive behaviour would be expected. The adsorption could therefore be made sufficiently selective to render possible the separation of enzymes acting on closely related substrates. This property, which cannot be explained at present, is also the only one which makes possible the separation of the enzymes that split sucrose and maltose respectively. The relation between the adsorptive actions of various alumina gels on solutions of a given enzyme, for instance, of saccharase, does not hold equally for any other enzyme, and is, for instance, quite different in the case of maltase. Thus there are varieties of alumina (β- and the meta-hydroxide) which are capable of taking up maltase comparatively readily from yeast autolysates, but saccharase only sparingly. In this way it is possible, even by a single application of the process, to obtain adsorbates, and from them again, by means of secondary alkali phosphate, solutions of enzymatically homogeneous maltase; at the same time the solutions of the saccharase are completely freed from maltase with little loss. The selective adsorption may be replaced by a process of selective elution from the adsorbates. By means of γ-alumina saccharase may be adsorbed together with maltase. Weakly alkaline or neutral phosphate solution then liberates both enzymes from the adsorbates, but a primary phosphate liberates saccharase completely and almost exclusively. The greater part of the maltase remains behind in a homogeneous condition and can be isolated by means of a secondary phosphate.

The adsorption of enzymes and their activators by various adsorbents is due to the qualitatively different affinities of single groups of atoms, and must be conceived to be similar to the action of an enzyme on its substrate. This dissimilar behaviour, utilised, for example, in the separation of saccharase from maltase, may, I believe, be attributed to differences in the chemical constitution of these enzymes and indeed to differences in their specific active groups.

In many cases there are indications as to which atomic groups of an enzyme are responsible for its union to an adsorbent. There are adsorbates of saccharase on alumina which under certain conditions hydrolyse sucrose just as rapidly as the saccharase contained in them would in free solution. On the other hand, the enzymatic activity of pancreatic lipase is to a large extent destroyed in its adsorbates on tristearin or on cholesterol. This suggests a participation of the specifically active group in the adsorption process. The lipase may be liberated again in an active condition from its almost inactive adsorbates. According to recent observations of E. Waldschmidt-Leitz and K. Linderström-Lang, enterokinase is inactive in the alumina adsorbate; its trypsin-binding group is occupied. On the other hand, the alumina adsorbates of trypsin and of trypsin-kinase are quite active.

The most delicate gradations in adsorptive power are determined by the peculiar chemical differentiation of the gels used, particularly of alumina, and by their preparation in a homogeneous state. Until quite recently the view prevailed that the gels of alumina precipitated from salts consist solely of aluminium oxide with adsorbed water and that their ageing results in a diminution of dispersivity, accompanied by a diminution of their adsorptive power. It is found, however, that the power of adsorbing saccharase increases rather than diminishes with the ageing of an alumina precipitate. The greater age of the gels brings about, not changes in dispersivity, but changes in chemical constitution. Under certain conditions the first aluminium hydroxide (α) may be isolated as an unstable gel of the formula $Al(OH)_3$. It changes in the course of a few hours into a second modification (β) and then very slowly into a third stable gel (γ), likewise of the composition $Al(OH)_3$. By heating it with ammonia to 250° there results yet another gelatinous aluminium hydroxide, the molecule of which contains less water; it corresponds to the formula AlO_2H. The chemical differences between these colloidal precipitates are very great, but there is no simple relationship between their basic and acid properties and their adsorptive powers. Inorganic chemistry will find a large field for the investigation of structure among such gelatinous hydroxides.

One of the results which we owe to the adsorption method is a knowledge of the enzymes in a higher state of purity. Most of the properties which had been ascribed to enzymes depended on their degree of purity and may be simulated, or deceptively altered, by accompanying substances, or at least influenced by them. The behaviour of an enzyme is thus influenced partly by quite foreign substances, accidentally associated with it in the course of the isolation, and partly by companions of physiological importance which co-operate with the enzyme when it occurs naturally. The influence of the accompanying substances extends to the stability of the enzymes, to the temperature of their destruction, to the temperature of their optimal activity, to their behaviour on adsorption, to their behaviour towards activators, inhibitors, and poisons, and even to the dependence of the reaction velocity on the hydrogen-ion concentration of the solution and on the concentration of the substrate.

With regard to both the control of the quantities of enzyme in preparative work and also a knowledge of the specificity of the enzymes, it is very important to remember that the comparison, by means of the reaction constant, of quantities of various enzyme preparations, of different origin and of different degrees of purity, may not be trustworthy. The relationship between the relative quantities of enzyme and the corresponding velocities may differ in various preparations of one and the same enzyme. And even when this relationship is constant, it is still uncertain whether equal velocities correspond to equal absolute quantities of enzyme in various solutions. In this respect some information is given by the dependence of the reaction velocity on the conditions of experiment. Since the fundamental investigations of S. P. L. Sörensen and of L. Michaelis and P. Rona, the dependence of the reaction velocity on the hydrogen-ion concentration of the enzyme solution has been recognised and taken into account. The measurement is usually carried out at the optimal p_H; a comparison is made between equal fractions (equal percentages) of the reaction velocities, maximal in relation to p_H. But even when there is a correspondence in the dependence on the p_H, the dependence of qualitatively similar enzyme preparations on the concentration of the substrate may still vary greatly as was shown in investigations made by R. Kuhn in my laboratory. At equal concentrations of the substrate, arbitrarily varying fractions of the maximal reaction velocity may be found. This varying dependence on p_S may be caused by inhibitors of the enzyme, accompanying substances which bind the specifically active group of the enzyme. The reaction velocities extrapolated for infinitely great substrate concentration then give a true measure of the quantities of enzyme. For this reason we propose reduced units of mass, for instance, for saccharases of different origin. The comparison of the velocities of fission at corresponding concentrations of the enzyme–substrate compound has made it possible to recognise more clearly the specificity of sugar- and glucoside-splitting ferments. Thus it has been ascertained that the hydrolysis of sucrose and of raffinose must be attributed to the same enzyme, saccharase (according to R. Kuhn); the hydrolysis of maltose and the various α-glucosides to the same maltase; and the hydrolysis of the various β-glucosides to the same β-glucosidase of emulsin. It may also happen that the accompanying substances do not attach themselves to the active group, but to other parts of the enzyme molecule, parts which are not directly concerned with the binding of the substrate. In many such cases the influence of qualitatively and quantitatively varying companions may be overcome by arbitrary additions, that is, by compensatory activation or by compensatory retardation, so that the quantities of the enzyme may be deduced with sufficient accuracy from the reaction velocities (estimation of the lipases).

The dependence of enzymic activity on p_H and p_S may vary according to the degree of purity of the enzyme. An example of the variability of the p_H optimum is afforded by the lipase of the stomach. In the human stomach, lipase, in contradistinction to pancreatic lipase, has the optimum action in the acid region, at p_H 5—6; the same applies to the stomach of the dog. The activity–p_H curve and the position of the optimum are constant for the unpurified lipase of any species, but this constancy is not a property of the enzyme itself. If this lipase is purified by an adsorption process with kaolin, an accompanying substance, which inhibits in alkaline solution, is removed, and apparently also a substance which activates in acid solution. After purification, human gastric lipase has the optimal activity in alkaline solution at $p_H = 8$.

The only property of the enzymes which is independent of the purity is, as far as we know, their qualitative specificity, their adaptation to a definite set of reactions determined by constitution and configuration. As the history of the proteases shows, this specificity remained indeterminable in certain cases, and was indeed determined incorrectly where the enzymes occurred in a non-homogeneous condition, as, for instance, erepsin together with trypsin, and as long as it was impossible to test them in a homogeneous condition. This specificity relating to chemical structure seems to be confined within narrow limits among the carbohydrates, but seems to be much less pronounced among the lipases and esterases. The lipatic enzymes of the pancreas, the liver, the stomach, etc., are adapted to the hydrolysis of higher and lower glycerides and of higher and lower esters of monohydric alcohols. The observations made hitherto have not necessitated the assumption that these enzymes are mixtures of the lipases proper with esterases. It seems rather that good esterases, such as that of the liver, are at the same time feeble lipases and that, conversely, good lipases, such as that of the pancreas, are esterases of low potency.

The determination of the specificity to chemical structure reveals the greatest degree of differentiation among the carbohydrases. It is even possible to ascertain the particular atomic group of the substrate molecule towards which the enzymic activity is directed. The enzymes which hydrolyse a compound sugar may attack the molecule in various places. This idea of assuming variously constituted intermediate reaction products in the enzymic fissions of the same substrate was first put forward by E. F. Armstrong (1904) in the case of the lactases of bitter almonds and of Kefir yeast. He found that the former is not appreciably inhibited by galactose, but strongly by glucose, whilst the latter is only influenced by galactose. The diversity in the points of attack and in the course of the reaction in the hydrolysis of the same compound sugar by hydrolytic enzymes was decisively shown in the investigations of saccharase by R. Kuhn and H. Münch (1923—26). Some saccharose-splitting enzymes react with the glucose half of this disaccharide (saccharase from *Aspergillus oryzæ:* gluco-saccharase inhibited by α-glucose); there are others, however, which exclusively attack the fructose portion of the molecule (saccharase from the usual laboratory yeasts: fructo-saccharase, inhibited by fructose). This sharp division of the various saccharases from animal organs, from fungi, and from higher plants into gluco- and fructo-saccharases seemed unjustifiable when H. von Euler and K. Josephson found that saccharase from Stockholm bottom yeast is also measurably inhibited by α-glucose. It could be shown, however, that the frequently occurring inhibition by α-glucose has nothing to do with the relation of the saccharase to saccharose, that the saccharase of the investigated yeasts possesses no affinity for α-glucose. The yeast saccharases in question hydrolyse all known gluco-derivatives of sucrose in which the fructose group, which determines the reaction with the enzyme, is intact, for instance, raffinose of the formula galactose<glucose<>fructose. On the other hand, R. Kuhn and G. E. von Grundherr found that melezitose of the formula glucose<fructose< >glucose is not attacked at all by yeast, but is hydrolysed by taka enzyme (gluco-saccharase).

A special case of specificity due to chemical structure is that caused by configuration. According to E. Fischer, this influence seems to be less pronounced among lipatic enzymes than among those that hydrolyse glucosides. The first example of stereochemical selection by a lipase occurs in an investigation by H. D. Dakin (1903—1905), who observed unequal rates of hydrolysis of the enantiomorphs of racemic esters of the mandelic acid group by means of an enzyme from liver. Such a preference for one enantiomorph enables us to distinguish all lipatic enzymes from one another. When I compared the action of a number of esterases, *viz.*, pancreatic, gastric, hepatic lipase, and taka-enzyme, on racemic esters of substituted phenylacetic acids, I found them all different in their selective action. Considering, however, the close association of lipases with activating companions, one is led to suspect that this specificity varies with the degree of purity. Hence this example is especially suitable for testing the question whether accompanying substances are responsible for the optical specificity or whether the lipases preserve their stereochemical peculiarities after purification. In an unpublished investigation (in conjunction with E. Bamann and J. Waldschmidt-Graser) it was found possible to increase the degree of purity of lipases considerably and to remove the associated substances which influence the reaction velocity. Gastric lipase (of the pig) was concentrated to 800—1000 times the original enzymic concentration, and thus freed completely from mucin-like admixtures. The stereochemical specificity of the purified lipatic enzyme remained, however, and still remains, qualitatively unchanged. It may, therefore, with a somewhat greater degree of probability than heretofore, be attributed to the enzyme itself.

Our views concerning the relations between enzymes or other catalysts and their substrates, between enzymes or other catalysts and their promoters and retarders, between enzymes and their adsorbents, depend on the assumption of affinities which cannot be formulated in the same way as the affinities in the constitutional formulæ and reaction equations of simpler organic compounds. The wide field of molecular affinities is not yet suitable for exact representation, nor has it yet been opened up to it. The lack of a strict formulation should not prevent us, however, from penetrating into this region of molecular forces and from collecting facts concerning the capacity of molecules to unite with one another. In view of the imperfection of our explanations, we may find support in the view of Faraday in his paper on the conservation of force (1858): "If in such strivings, we . . . see but imperfectly, still we should endeavour to see, for even an obscure and distorted vision is better than none. Let us, if we can, discover a new thing *in any shape*: the true appearance and character will be easily developed afterwards."

CXCII.—*The Diacyl Derivatives of Benzidine and* p-*Phenylenediamine.*

By Francis Joseph Anthony Brogan.

An alternation in melting point such as that shown by successive members of the normal fatty acid series has been found by Robertson (J., 1908, **93**, 1033; 1919, **115**, 1210) to occur to a more marked extent in the amides and various substituted amides; for the odd and the even members of each series, two distinct curves, more or less parallel, were obtained when the melting points were plotted against the number of carbon atoms in the acid chain. To explain this alternation of physical properties, the theory of alternating polarities has been put forward.

The melting points of two series of diacyl diamines, prepared by condensing the normal fatty acid chlorides with benzidine and *p*-phenylenediamine, respectively, have now been determined.

The diacyl diamines, with the exception of the diacetyl compounds, were prepared by the general method described by Robertson (*loc. cit.*). Dipropionyl- and dibutyryl-*p*-phenylenediamine could not be isolated, owing probably to their extreme solubility, but small amounts of the monoacyl compounds were obtained by adding light petroleum to aqueous-alcoholic solutions of the crude products. Recrystallisation of the crude product from aniline also gave the monoacyl compound.

The diacetyl compounds were prepared from acetic anhydride and the base in aqueous-alcoholic solution by Cain's method (J., 1909, **95**, 714). A considerable proportion of monoacyl compound also was formed.

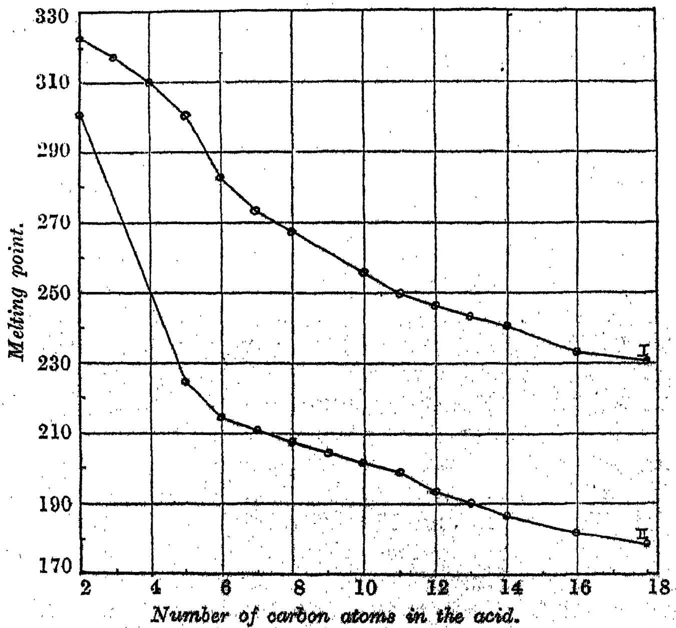
The crude products were recrystallised until the melting points were constant. The benzidine compounds, with the exception of the first three or four members of the series, are sparingly soluble in most of the common solvents. Alcohol was found to be the most suitable solvent for most of them, but the rate of solution was very slow, and prolonged boiling with a large volume of alcohol was necessary. Diacetylbenzidine crystallised well from aniline. The dipropionyl and dibutyryl compounds were very soluble in alcohol, and required to be precipitated by water. The four highest members were recrystallised from amyl acetate or acetic acid. The *p*-phenylenediamine derivatives, with the exceptions mentioned below, were recrystallised from alcohol, the solubility being much greater than that of corresponding compounds in the benzidine series. The diacetyl compound was recrystallised from nitrobenzene, and the two highest members from amyl acetate.

The new compounds prepared in this investigation, with their formulæ, melting points, and analytical results, are tabulated below.

Benzidine derivs.	M. p.	% N found.	*p*-Phenylenediamine derivs.	M. p.	% N found.
Dipropionyl, $C_{18}H_{20}O_2N_2$	317°	9·3	Divaleryl, $C_{16}H_{24}O_2N_2$	225°	10·3
Dibutyryl, $C_{20}H_{24}O_2N_2$	310	8·4	Dihexoyl, $C_{18}H_{28}O_2N_2$	215	9·1
Divaleryl, $C_{22}H_{28}O_2N_2$	301	7·7	Diheptoyl, $C_{20}H_{32}O_2N_2$	211	8·3
Dihexoyl, $C_{24}H_{32}O_2N_2$	283	7·3	Dioctoyl, $C_{22}H_{36}O_2N_2$	208	7·7
Diheptoyl, $C_{26}H_{36}O_2N_2$	274	6·7	Dinonoyl, $C_{24}H_{40}O_2N_2$	205	7·0
Dioctoyl, $C_{28}H_{40}O_2N_2$	268	6·4	Didecoyl, $C_{26}H_{44}O_2N_2$	202	6·6
Didecoyl, $C_{32}H_{48}O_2N_2$	256	5·5	Diundecoyl, $C_{28}H_{48}O_2N_2$	199	6·5
Diundecoyl, $C_{34}H_{52}O_2N_2$	250	5·4	Dilauryl, $C_{30}H_{52}O_2N_2$	194	5·9
Dilauryl, $C_{36}H_{56}O_2N_2$	247	4·9	Ditridecoyl, $C_{32}H_{56}O_2N_2$	190	5·6
Ditridecoyl, $C_{38}H_{60}O_2N_2$	243	4·9	Dimyristyl, $C_{34}H_{60}O_2N_2$	187	5·3
Dimyristyl, $C_{40}H_{64}O_2N_2$	241	4·6	Dipalmityl, $C_{38}H_{68}O_2N_2$	182	4·8
Dipalmityl, $C_{44}H_{72}O_2N_2$	233	4·3	Distearyl, $C_{42}H_{76}O_2N_2$	178	4·5
Distearyl, $C_{48}H_{80}O_2N_2$	231	4·1			

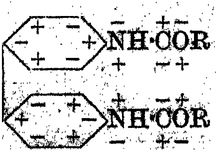
The results are shown graphically in the diagram, in which the melting points are plotted against the number of carbon atoms in the substituting acid. The general nature of the curves is typical, in so far as they fall fairly sharply at first and then more regularly with increase of molecular weight, but alternation is entirely absent. It is remarkable also that no minimum melting point is reached even at the eighteenth member, although a slight flattening is apparent about this point. Robertson's results indicate that the melting points become higher and the minimum occurs later as the molecule becomes heavier.

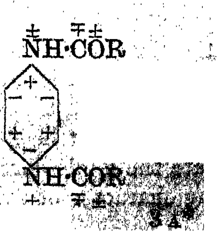
FIG. 1.



I. *Benzidine derivatives.* II. p-*Phenylenediamine derivatives.*

An examination of the polarity of the diacyl benzidines and *p*-phenylenediamines reveals the fact that a system of "crossed polarities" similar to that existing in the dibasic acids with an even number of carbon atoms is present.





This, together with the highly symmetrical nature of the molecule, would contribute to the structural stability of the acid, and thus tend to make the melting point high. The heaping up of like charges as in the odd dibasic acids, which may be supposed to make the crystalline arrangement less stable, and the melting points lower than those of the even acids, does not occur in the above compounds; this may explain the absence of alternation.

In conclusion, I wish to thank Professor Robertson for valuable advice and criticism in connexion with this research.

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[*Received, April 27th*, 1927.]

CXCIII.—*Aromatic Sulphonyl Disulphides.*

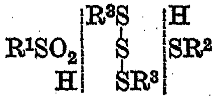
By LESLIE GEORGE SCOTT BROOKER, REGINALD CHILD, and SAMUEL SMILES.

THE relative stability of incompletely oxidised sulphur chains attached to aromatic nuclei has not yet been systematically examined. Facts available from various sources show that so far as the dithio-system is concerned the fully oxidised chain of the disulphones is more resistant to fission than the partly oxidised group in the thiolsulphonates or in the unoxidised chain of disulphides. These relations, considered together with the labile character of the disulphide group in the tetrathio-compounds, $ArSO_2{\cdot}S_2{\cdot}SO_2Ar$, which spontaneously lose sulphur, yielding the corresponding monosulphides (Otto and Troger, *Ber.*, 1891, 24, 1125), led to attempts to devise a method of introducing the thiolsulphonate group similar to that recently devised for inserting the thioaryl group (J., 1926, 1723). The experiments hitherto made with this object have chiefly dealt with the fission of substances containing the partly oxidised system $ArSO_2{\cdot}S{\cdot}S$— and have been devised to determine the mode of fission of this sulphur chain. If, as appeared probable for reasons such as those stated, the dithio-linking proved to be the less stable point of the sulphur complex, an intact thiolsulphonate group might survive the attack of suitable agents. The present investigation deals mainly with the diaryl sulphonyl disulphides. Although the desired method of synthesis of disulphoxides has not yet been attained, the results are now described, since this class of substance has not been previously encountered and their reactions illustrate the labile character of this type of sulphur chain and the varying character of the decomposition products. The substances in question are readily obtained from the reaction of an aryl thiolsulphonate with a sulphur chloride,

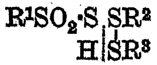
$$ArSO_2{\cdot}SNa + SClAr = NaCl + ArSO_2{\cdot}S{\cdot}SAr,$$

and are well-defined materials which may be purified by the usual methods but decompose near their temperatures of fusion. Attempts to obtain these substances by partial oxidation of the more stable of the aromatic trisulphides or by reaction of a sulphinate with a disulphur chloride have not yet been successful. The sulphur chain in the aryl sulphonyl disulphides is easily broken by mercaptans, the chief product being the trisulphide corresponding to the mercaptan used (I). At the same time, fission of the dithio-system takes place in the reverse manner with the result that, when the aryl group of the mercaptan used is different from those present in the sulphonyl disulphide, unsymmetrical disulphides are formed (II). These modes of fission are summarised as follows :

(I.)



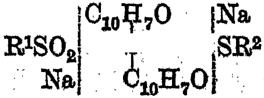
$$\begin{array}{r|c|l} & R^3S & H \\ R^1SO_2 & S & SR^2 \\ H & SR^3 & \end{array}$$



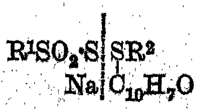
$$\begin{array}{r|l} R^1SO_2{\cdot}S & SR^2 \\ H & SR^3 \end{array}$$

(II.)

(III.)



$$\begin{array}{r|c|l} & C_{10}H_7O & Na \\ R^1SO_2 & & SR^2 \\ Na & C_{10}H_7O & \end{array}$$



$$\begin{array}{r|l} R^1SO_2{\cdot}S & SR^2 \\ Na & C_{10}H_7O \end{array}$$

(IV.)

With sodium 2-naphthoxide or the sodium derivative of acetylacetone the unsymmetrical monosulphides are obtained (IV) together with 2-naphthol sulphide in the case of the first-named reagent (III), but since sodium mercaptide is liberated during these decompositions the symmetrical disulphide which is formed according to (II) is usually also encountered.

The behaviour of these reagents with the diarylsulphonyl monosulphides and trisulphides is similar. Thus ditoluenesulphonyl trisulphide was almost quantitatively decomposed by sodium 2-naphthoxide to 2-naphthol sulphide and toluenethiolsulphonate,

$$RSO_2{\cdot}S_3{\cdot}SO_2R \xrightarrow[C_{10}H_7{\cdot}ONa]{} 2RSO_2{\cdot}SNa + (C_{10}H_6{\cdot}OH)_2S,$$

and by sodium mercaptide to the trisulphide,

$$RSO_2{\cdot}S_3{\cdot}SO_2R \xrightarrow[R^1SNa]{} R^1{}_2S_3 + 2RSO_2{\cdot}SNa.$$

Ditoluenesulphonyl sulphide yielded 2-naphthol sulphide and the sulphinate

$$(RSO_2)_2S \xrightarrow[C_{10}H_7{\cdot}ONa]{H_2O} 2RSO_2Na + (C_{10}H_6{\cdot}OH)_2S.$$

The trisulphides, sulphonyl disulphides and disulphonyl monosulphides form an interesting series in which the trithio-system occurs in successive stages of oxidation, but at present it is inadvisable to discuss the relative stability of these, since experience has shown that in each class this may vary with the nature of the substituents in the aromatic nuclei, and precise information concerning this factor is lacking.

EXPERIMENTAL.

The sulphonyl disulphides were prepared by shaking the finely powdered potassium thiolsulphonate with dry ether containing the theoretical amount of aryl sulphur chloride. Interaction was usually rapid and when it was complete the solid was collected and washed with water; the residue, containing the desired material, was then purified from a suitable solvent. A further quantity of the sulphonyl disulphide could in most cases be obtained from the ethereal solution. In this way, the following derivatives were obtained; they are numbered for the purpose of reference on a subsequent page.

I. 4-*Toluenesulphonyl* 2-*nitrophenyl disulphide*,

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

formed yellow plates, m. p. 141°, from acetic acid (Found: S, 28·3; *M*, 336. $C_{13}H_{11}O_4NS_3$ requires S, 28·2%; *M*, 341).

II. 4-*Acetamidobenzenesulphonyl* 2-*nitrophenyl disulphide*,

$$NHAc{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

separated from acetone in yellow needles, m. p. 171° (decomp.) (Found: C, 43·8; H, 3·1; S, 24·9. $C_{14}H_{12}O_5N_2S_3$ requires C, 43·7; H, 3·1; S, 25·0%).

III. 4-*Toluenesulphonyl* 4-*chloro*-2-*nitrophenyl disulphide*,

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_3Cl{\cdot}NO_2,$$

was obtained from hot alcohol in yellow needles, m. p. 114° (Found: C, 41·6; H, 2·9; Cl, 9·3; S, 25·5. $C_{13}H_{10}O_4NClS_3$ requires C, 41·5; H, 2·9; Cl, 9·4; S, 25·6%).

IV. 4-*Toluenesulphonyl* 2 : 5-*dichlorophenyl disulphide*,

$$C_7H_7{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_3Cl_2,$$

separated from benzene–light petroleum in prisms, m. p. 95—96° (Found: C, 42·7; H, 2·7; Cl, 19·3; S, 26·1. $C_{13}H_{10}O_2Cl_2S_3$ requires C, 42·7; H, 2·8; Cl, 19·4; S, 26·3%).

V. 4-*Methoxytoluene*-3-*sulphonyl* 2-*nitrophenyl disulphide*,

$$MeO{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

has m. p. 115—116° (Found: C, 45·2; H, 3·7; S, 25·4; *M*, 362. $C_{14}H_{13}O_5NS_3$ requires C, 45·2; H, 3·5; S, 25·9%; *M*, 371).

VI. 4-*Chlorobenzenesulphonyl* 2-*nitrophenyl disulphide*,

$$C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

formed yellow plates from acetic acid; m. p. 147° after softening at about 130° (Found: C, 39·9; H, 2·4; Cl, 9·9; *M*, 352. $C_{12}H_8O_4NClS_3$ requires C, 39·8; H, 2·2; Cl, 9·8%; *M*, 361·5).

The interaction of these substances with the reagents mentioned was effected in boiling alcohol which contained two molecular proportions of the mercaptan or sodium 2-naphthoxide and one of the sulphonyl disulphide. When the reaction was complete, the alcohol was evaporated and the residue was extracted with water. The further separation of the products varied according to the nature of the reactants. Identification of the products was effected by comparison with authentic specimens from other sources; when the substances had not been previously described, they were prepared for comparison by other methods. In the following summary the numerals refer to the sulphonyl disulphides described above.

I, with the sodium derivative of acetylacetone, yielded 2-nitrophenyl disulphide and 2-nitrophenyl acetylacetonyl sulphide, m. p. 136—137° (J., 1926, 1727). From the interaction with 2 : 5-dibromophenyl mercaptan the corresponding trisulphide and 2 : 5-dibromophenyl 2-nitrophenyl disulphide were isolated. 2 : 5-*Dibromophenyl trisulphide*, m. p. 167—168°, formed needles from benzene (Found : Br, 56·5. $C_{12}H_6Br_4S_3$ requires Br, 56·5%) and was also prepared from the mercaptan and sulphur dichloride in carbon tetrachloride. 2 : 5-*Dibromophenyl 2-nitrophenyl disulphide*, $C_6H_3Br_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$, was also obtained from the dibromophenyl mercaptan and 2-nitrophenyl sulphur chloride. It formed yellow prisms, m. p. 138°, from acetic acid (Found : Br, 38·1. $C_{12}H_7O_2NBr_2S_2$ requires Br, 38·0%).

III, with sodium 2-naphthoxide, yielded 2-naphthol sulphide, toluenesulphinic acid, 4-chloro-2-nitrophenyl disulphide, and 4-chloro-2-nitrophenyl 2-naphthol sulphide (I) (Found : Cl, 10·3. Calc. : Cl, 10·7%).

IV, with 2-nitrophenyl mercaptan, gave 2-nitrophenyl trisulphide (Lecher, *Ber.*, 1922, **55**, 2423) and 2 : 5-*dichlorophenyl 2-nitrophenyl disulphide*, $C_6H_3Cl_2{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$, which was also prepared from 2-nitrophenyl sulphur chloride and 2 : 5-dichlorophenyl mercaptan, and separated from hot acetic acid in yellow needles, m. p. 138° (Found : C, 43·3; H, 2·1. $C_{12}H_7O_2NCl_2S_2$ requires C, 43·2; H, 2·2%).

V, with 2 : 5-dichlorophenyl mercaptan, yielded 2 : 5-dichlorophenyl 2-nitrophenyl disulphide, 4-methoxytoluene-3-sulphinic acid, and 2 : 5-*dichlorophenyl trisulphide*, $(C_6H_3Cl_2)_2S_3$, which formed needles, m. p. 140°, from acetic acid (Found : Cl, 36·2. $C_{12}H_6Cl_4S_3$ requires Cl, 36·5%). This substance was also obtained from the mercaptan and sulphur chloride; by hydrogen peroxide in acetic acid at 100°, it was converted into 2 : 5-dichlorophenyl disulphoxide.

VI, with the sodium derivative of acetylacetone, yielded 2-nitrophenyl disulphide, 4-chlorobenzenesulphinic acid, and 2-nitrophenyl acetylacetonyl sulphide.

4-Toluenesulphonyl trisulphide or 4-toluenesulphonyl sulphide was decomposed in boiling alcohol by sodium 2-naphthoxide (2 mols.). The products were as stated in the theoretical part. Sodium 4-toluenethiolsulphonate, formed from the first-named sulphide, was identified by conversion into 4-toluenesulphonyl 4-chloro-2-nitrophenyl disulphide.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us (L. G. S. B.) to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, April 28th,* 1927.]

CXCIV.—*The Dicarbazyls. Part III. The Oxidation of Carbazole and* N-*Alkylcarbazoles in Acid Solution.*

By PETER MAITLAND and STANLEY HORWOOD TUCKER.

PERKIN and TUCKER (J., 1921, **119**, 216) have described three products of the oxidation of carbazole by potassium permanganate in acetone solution. Two of these were crystalline, A, m. p. 220°, and B, m. p. 265°, and the third amorphous, m. p. about 175°. A and B were proved to be dicarbazyls, the constitutions, however, being unknown; neither is 3 : 3′-dicarbazyl, since synthesised by Tucker (J., 1926, 3033). McLintock and Tucker (this vol., p. 1214) have shown that A is 9 : 9′-dicarbazyl.

In the present research, by oxidising 9-methylcarbazole, we made sure that, in any dicarbazyl produced, the two carbazole nuclei would be united by a bond between two carbon atoms. 9-Methylcarbazole was unaffected in acetone solution by potassium permanganate. Oxidation by Wieland's method (*Ber.*, 1913, **46**, 3296), however, gave 9 : 9′-dimethyl-3 : 3′-dicarbazyl, the constitution of which was proved by its preparation from 3 : 3′-dicarbazyl by direct methylation. These results were confirmed by analogous experiments on 9-ethylcarbazole, 9 : 9′-diethyl-3 : 3′-dicarbazyl being obtained. In both these oxidations there was no evidence of the formation of any isomeric 1 : 1′- or 1 : 3′-dicarbazyl.

The fact that no 3 : 3′-dicarbazyl was formed in Perkin and Tucker's oxidation of carbazole led us to attempt the oxidation by other methods. Carbazole, when oxidised in boiling acetic acid with sodium dichromate, gave a product which contained chromium. When, however, the :NH group was protected by sulphuric acid, no chromium-containing products were obtained. Although no sulphate of carbazole has been isolated, it appears to exist under the experimental conditions employed, since oxidation by Wieland's method gave 3 : 3′-dicarbazyl, uncontaminated with any 9 : 9′-dicarbazyl.

The mechanism of the acid oxidation of carbazole was thought to be closely allied to that of the corresponding oxidation of diphenylamine to diphenylbenzidine (Wieland, *Ber.*, 1913, **46**, 3296. *o*-Nitrodiphenylamine gives, correspondingly, *NN′*-di-*o*-nitrophenylbenzidine; Tucker, *loc. cit.*, 3034). Two theories of the mechanism of this oxidation have been put forward : (1) That the benzene nuclei unite directly, without the formation of an intermediate product (Wieland); (2) that the primary attack occurs at the :NH group with the formation of an intermediate compound which subsequently undergoes transformation (Marqueyrol and Muraour, *Bull. Soc. chim.*, 1914, **15**, 191).

(1) In support of this assumption, Wieland has shown that tetraphenylbenzidine is formed by the oxidation of triphenylamine. This evidence is not conclusive, because the oxidation is effected in acetic acid solution, whereas in the case of diphenylamine the presence of sulphuric acid is necessary, and also because of the introduction of the acidic phenyl group. We have, however, been able to oxidise *N*-methyldiphenylamine in sulphuric acid solution to *NN′*-dimethyldiphenylbenzidine, $\mathrm{NMePh{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NMePh}$. The intermediate formation of an N—N-compound is here excluded; oxidation brings about direct C—C-linking. This is in complete agreement with Wieland's view.

(2) The investigations of Marqueyrol and Muraour have led them to the conclusion that the sulphuric acid is only necessary, in that it causes the transformation of an intermediate product. (The constitution of this intermediate product is unknown, but it has been shown that it cannot be tetraphenylhydrazine.) They base their conclusions on oxidation experiments in which they protected the NH group by varying quantities of concentrated sulphuric acid, and found that the amount of recovered diphenylamine increased with increase in the amount of concentrated sulphuric acid used. We have repeated their experiments, and have found that the amount of unchanged diphenylamine is negligible. There seems, therefore, to be no valid experimental work against the view of Wieland. Furthermore, in the analogous acid oxidation of carbazole to give 3 : 3′-dicarbazyl, the evidence is against the intermediate formation of 9 : 9′-dicarbazyl, since the transformation of 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl cannot be brought about (McLintock and Tucker, *loc. cit.*). Again, the oxidation of 9-methyl-

and of 9-ethyl-carbazole to the corresponding 3 : 3′-dicarbazyl derivatives cannot take place through the intermediate formation of a 9 : 9′-dicarbazyl.

In all the acid oxidations of carbazole and its derivatives, and also in the acid oxidation of *N*-methyldiphenylamine, brightly coloured substances are produced. We suggest that these substances possess quinonoid structures, and are similarly constituted to the analogously formed oxidation products of diphenylamine (Kehrmann and Micewicz, *Ber.*, 1912, **45**, 2641).

EXPERIMENTAL.

Oxidation of 9-*Methylcarbazole by Wieland's Method* (*modified*).—Methylcarbazole (5 g.) was dissolved in a mixture of glacial acetic acid (200 c.c.) and sulphuric acid (5 c.c.), and sodium dichromate (6·5 g.; 1½ times the theoretical quantity) dissolved in the smallest quantity of water was added during 1 minute, the whole being cooled in ice. The solution turned bluish-green immediately, and a precipitate formed. After 10 minutes, the solution was poured into an equal bulk of a concentrated solution of sodium bisulphite, and heated on the water-bath until the blue colour disappeared. The green precipitate obtained was removed and extracted with benzene; the residue (0·5 g.) contained chromium. The concentrated, hot benzene solution was poured into twice its volume of hot alcohol to remove unchanged 9-methylcarbazole. The light brown, crystalline mass, deposited over-night, was dissolved in hot acetic anhydride, and glacial acetic acid added, followed by zinc dust. After boiling for 10 minutes, the dark brown solution lightened in colour; it was filtered, and the filtrate poured cautiously into ammonia solution (ammonia, *d* 0·88, diluted with its own bulk of water). The slightly coloured mass deposited was crystallised three times from benzene (charcoal). Slightly pink needles of 9 : 9′-*dimethyl*-3 : 3′-*dicarbazyl*, m. p. 200—202°, were obtained (Found: C, 86·4; H, 5·6; N, 7·8; *M*, cryoscopic in benzene, 380, 375. $C_{26}H_{20}N_2$ requires C, 86·7; H, 5·6; N, 7·8%; *M*, 360).

Oxidation of 9-*Ethylcarbazole.*—9-Ethylcarbazole (20 g.), glacial acetic acid (1 litre), sulphuric acid (25 c.c.), and sodium dichromate (12·8 g.) were used as in the preceding oxidation. The residue (2 g.) after the extraction with benzene contained chromium. The benzene solution was concentrated and poured into hot alcohol (400 c.c.). The brown, crystalline mass deposited over-night (16 g.) melted at 174—176°. It was purified as described above and cream-coloured prisms of 9 : 9′-*diethyl*-3 : 3′-*dicarbazyl*, m. p. 188—190°, were obtained (Found: C, 86·5; H, 6·4; N, 7·2; *M*, by Rast's method, 342, 391. $C_{28}H_{24}N_2$ requires C, 86·6; H, 6·2 N, 7·2%; *M*, 388).

Excellent yields of the crude alkylated dicarbazyls were obtained, but great difficulty was experienced in isolating the pure dicarbazyls. Fractional crystallisation from benzene, toluene, xylene, acetic anhydride, or pyridine, in which the dicarbazyls are very soluble, and also from acetic acid, alcohol, or acetone, in which they are sparingly soluble, was tried in the attempt to isolate an isomeride. Sublimation in a vacuum or treatment with potassium permanganate in acetone solution had little effect. There was no evidence of the presence of any 1 : 1′- or other isomeride.

Oxidation of Carbazole.—The procedure used in the oxidation of 9-methylcarbazole (above) was followed, pure carbazole (5 g.), glacial acetic acid (1250 c.c.), sulphuric acid (30 c.c.), and sodium dichromate (3·2 g.) being employed. After the heating following the addition of the bisulphite (1 litre), the solution was further diluted and left over-night. The light brown, flocculent precipitate was washed, dried, and extracted with anisole (500 c.c.); the green residue (1 g.) did not contain chromium. The dark brown filtrate was concentrated and boiled with charcoal; 3 : 3′-dicarbazyl (1·7 g.), m. p. over 300°, was then obtained in colourless microcrystals. Its acetyl derivative was identical with that of synthetic 3 : 3′-dicarbazyl (Tucker, *loc. cit.*).

Methylation of 3 : 3′-*Dicarbazyl* (Stevens and Tucker's method, J., 1923, **123**, 2140).—3 : 3′-Dicarbazyl (0·8 g.) was suspended in acetone (40 c.c.), methyl sulphate (2 c.c.) added, and then powdered potassium hydroxide (2 g.). Water was added drop by drop until the potash formed a layer. After boiling for 10 minutes, the solution was poured into water, and the precipitate obtained was washed, dried, and crystallised from benzene three times, giving white needles, m. p. 198—200°. This substance was identical with 9 : 9′-dimethyl-3 : 3′-dicarbazyl prepared by oxidation of 9-methylcarbazole.

Ethylation of 3 : 3′-*Dicarbazyl.*—3 : 3′-Dicarbazyl (0·4 g.) was suspended in acetone (30 c.c.), and ethyl sulphate (5 c.c.) added; powdered potassium hydroxide (10 g.) was then added in small quantities to the boiling solution. On pouring the mixture into water, an oil was obtained (due to the large amount of potash acting on the acetone). After steam distillation, the solid residue was crystallised four times from benzene, and shown to be 9 : 9′-diethyl-3 : 3′-dicarbazyl.

Oxidation of N-*Methyldiphenylamine.*—*N*-Methyldiphenylamine (prepared as described by Gibson and Vining, J., 1923, **123**, 835, and further purified by steam distillation) (5 g.) was dissolved in a cold mixture of concentrated sulphuric acid (20 c.c.) and water (50 c.c.). To the pale yellow solution, sodium dichromate (1·35 g.), dissolved in water (10 c.c.), was added drop by drop with shaking. A reddish-violet coloration was produced, but was rapidly discharged, and a white precipitate separated. Decoloration was more rapid as the solution became warm. When the last few drops of the dichromate solution had been added (*i.e.*, slight excess over the amount theoretically required), the mauve colour persisted. The colour was removed by treating the mixture with a few drops of sulphurous acid. The separated, salmon-coloured substance (5 g.) was extracted with benzene. Part remained insoluble. The concentrated benzene extract deposited faintly green crystals, which, after several recrystallisations from benzene and finally from acetone, gave white, nacreous laminæ, softening at 167° and melting at 170°, of NN'-*dimethyldiphenylbenzidine* (Found: C, 85·9; H, 6·8; N, 7·9; *M*, by Rast's method, 386. $C_{26}H_{24}N_2$ requires C, 85·7; H, 6·6; N, 7·7%; *M*, 364). On account of the necessary repeated crystallisations the yield of pure product (1·5 g.) was low. No isomeride could, however, be isolated. Crystallisation from ethyl acetate or acetone, without previous use of benzene, failed to purify the product. All solutions possess a faint violet fluorescence.

It crystallises from the usual organic solvents, but is insoluble in alcohol or light petroleum.

N-Methyldiphenylamine, by oxidation with potassium permanganate in acetone, gave *NN'*-dimethyldiphenylbenzidine in small yield.

Methylation of Diphenylbenzidine.—*NN'*-Diphenylbenzidine (1 g.) was dissolved in methyl sulphate (10 c.c.) by warming on the water-bath for 15 minutes. A solution of sodium carbonate in water (35 g. in 200 c.c.) was added during 1 hour, the temperature being kept between 50° and 60°. An oil separated and solidified on cooling. After being washed and dried, the solid was extracted with benzene. Crystals eventually obtained were identical with those of *NN'*-dimethyldiphenylbenzidine prepared by oxidation of *N*-methyldiphenylamine.

UNIVERSITY OF GLASGOW. [*Received, April 22nd*, 1927.]

CXCV.—*Acid Soaps: A Crystalline Potassium Hydrogen Dioleate.*

By JAMES WILLIAM MCBAIN and ALEXANDER STEWART.

No acid soaps of definite composition have been shown to exist, although the analogous acid sodium acetates ($NaC_2H_3O_2,C_2H_4O_2$, and $NaC_2H_3O_2,2C_2H_4O_2$) have long been known. The present paper describes the preparation of the first definite crystalline compounds of this type observed with the soaps.

Potassium hydrogen dioleate was first prepared from oleic acid "Kahlbaum" and a special Kahlbaum preparation of potassium oleate. These were dissolved in distilled alcohol, and upon cooling with ice a crystalline deposit was obtained. Two or three recrystallisations completely removed any brown colour. The crystals were dried, after being washed with ice-cold alcohol, in a vacuum desiccator over fused calcium chloride for 8—10 days; they then attained constant weight and the analysis was not altered by further drying at 40° in a vacuum.

The acid soap was analysed as follows. To a weighed quantity of solution contained in a stoppered flask a measured excess of standard hydrochloric acid was added slowly from a pipette with vigorous stirring. The precipitated fatty acid was allowed to stand over-night, for the resulting emulsion to clear, and then filtered off through wetted filter-paper and washed free from hydrochloric acid with boiled-out distilled water. The filtrate was titrated with standard sodium hydroxide and phenolphthalein; the difference between this and the amount of hydrochloric acid originally taken determines the total concentration of soap and hydroxide. The fatty acid on the filter paper was dissolved in boiled-out alcohol and titrated with sodium hydroxide, which had been standardised both against the oleic acid used and against hydrochloric acid (Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 345), more boiled-out alcohol being added, if necessary, in order to maintain an alcohol concentration of 70—80%. Determinations of saponification value gave results in good agreement with this method of analysis.

The procedure ultimately adopted was to obtain crystals of acid soap from alcoholic solutions containing various proportions of potassium oleate and oleic acid. The analyses in the table show that the crystals contained one equiv. of oleic acid to one equiv. of potassium oleate, and that the composition over a wide range was independent of the proportions in the alcohol. In each case, 3—4 g. of acid soap were taken for analysis and about 6 g. for saponification values. The amounts of oleate and potassium found by analysis agreed with the total weight of sample taken within 0·2%.

Analysis of crystals obtained from alcoholic solutions of potassium oleate and oleic acid in various proportions.

Propn. in alc.	Ratio in crystal (Oleate/K).	Mol. wt. from saponification value.
KOl : 2HOl.	2·011	—
KOl : HOl.	2·007, (1·952), 1·980, 1·990, 1·986, 2·006, 2·005	600, 600·4
2KOl : HOl.	—	602·6, 601·9
3KOl : HOl.	—	903·1, 905·7

Theory for KOl : HOl = 602·6
" " 2KOl : HOl = 923·1

The following method of preparation was found convenient: 130 G. of oleic acid and 145 g. of potassium oleate are dissolved in alcohol by warming, diluted to a litre, and allowed to crystallise at 0°. The white crystals are recrystallised 3 or 4 times—the last time only, from dry alcohol. Drying is completed in a vacuum over frequently-changed fused calcium chloride. This process not only removes the colour, if impure oleic acid is used, but results in definite purification.

The acid soap may be recrystallised from pure oleic acid instead of alcohol; the ratio of oleate to potassium in such a recrystallised product, dried in a screw press with renewed layers of filter paper, was found by analysis to be 2·026 and 2·004.

Potassium hydrogen dioleate forms well-defined crystalline plates; the photograph (Fig. 1) shows a typical group of crystals with dark-ground illumination. This compound possesses a transition point at 43°, at which temperature the solid partly liquefies, and it is only upon heating the system to above 107° that it again becomes homogeneous, giving a clear liquid.

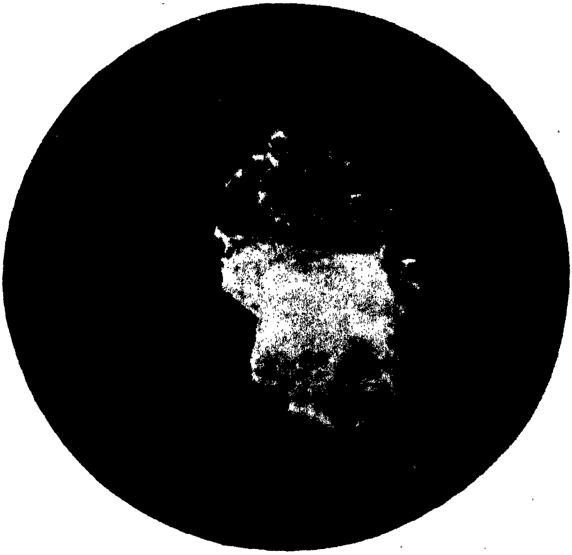
In order to determine whether potassium oleate or a second acid soap was the decomposition product, a quantity of the crystals was placed in a screw press between a number of filter-papers, and kept in an oven at 55—60°, the filter-papers being changed until no more oily liquid was removed from the press cake. Analysis of the product showed that the ratio of oleate radical to potassium was 1·001. Thus the decomposition product at 55° is neutral potassium oleate, the other phase being a liquid solution of potassium oleate in oleic acid.

Further communications will contain the results of phase-rule investigations in the two-component systems soap–fatty acid and the three-component systems soap–fatty acid–water.

Summary.

A definite crystalline compound, anhydrous potassium hydrogen dioleate, has been obtained, showing a transition point at 43° at which it breaks up into potassium oleate and a liquid solution of oleate and oleic acid. It crystallises unaltered from oleic acid or from various compositions of alcoholic solution. It offers a means of purification of oleic acid.

UNIVERSITY OF BRISTOL. [*Received, December 20th,* 1926.]



Crystal of potassium hydrogen dioleate. Oblique illumination. Magnification × 100.

[*To face p.* 1394.]

CXCVI.—*The Action of Nitrous Acid on Substituted* p-*Phenylenediamines. Part I. Benzyl*-n-*butyl*-p-*phenylenediamine.*

By JOSEPH REILLY and PETER J. DRUMM.

BUTYL-*p*-PHENYLENEDIAMINE behaves normally on diazotisation (Reilly and Hickinbottom, J., 1917, **111**, 1034). According to Hantzsch (*Ber.*, 1902, **35**, 896), methyl-*p*-phenylenediamine cannot be readily diazotised in hydrochloric acid solution, nitrogen being evolved even below 0°; the present authors have found, however, that a much more stable diazo-solution is obtained if sulphuric acid is used. Substituents in aromatic diamines therefore have a marked influence on the stability of the diazo-solutions produced from them, and in view of this the authors have commenced an investigation on the nature of the reaction between nitrous acid and various mono- and di-substituted diamines and on the stability of the resulting solutions.

Benzyl-n-*butyl*-p-*phenylenediamine*, $NH_2\cdot C_6H_4\cdot N(C_4H_9)\cdot CH_2Ph$, the first diamine to be investigated, was obtained from *benzyl*-n-*butylaniline* through the p-*nitroso*-compound and also by reduction of the azo-compound formed by coupling this tertiary amine with diazosulphanilic acid. It diazotises readily to give a comparatively stable diazo-solution.

EXPERIMENTAL.

Benzyl-n-*butylaniline.*—Benzylaniline (1 mol.) and *n*-butyl iodide (1 mol.) were heated together at 100° for 6 hours, the excess of *n*-butyl iodide was removed under diminished pressure, and the residue made alkaline with aqueous sodium hydroxide. The resulting oil was dissolved in ether and dried with potassium carbonate. The fraction, b. p. 190—200°/17 mm., on refractionation gave *benzyl*-n-*butylaniline* as a pale yellow oil, b. p. 193—195°/17 mm., $d^{16\cdot 5°}$ 1·005 (yield, 20%). It possesses feebly basic properties and is very sparingly soluble in dilute acids. The *picrate* forms bright yellow prisms, m. p. 129° (Found: $C_6H_3O_7N_3$, 49·3. $C_{17}H_{21}N,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 48·9%), and is decomposed by boiling water. The *chloroplatinate* is only slightly soluble in alcohol, from which it separates in biscuit-coloured prisms, m. p. 185—186° (decomp.) [Found: Pt, 21·8. $(C_{17}H_{22}N)_2PtCl_6$ requires Pt, 21·9%].

p-*Nitrosobenzyl*-n-*butylaniline.*—A well-cooled solution of benzyl-*n*-butylaniline in glacial acetic acid was slowly treated with a solution of the theoretical quantity of sodium nitrite in the minimum of water. The mixture was stirred for 3 hours and then diluted with ice-water, and the precipitated green oil was dissolved in benzene. From the dried, cooled benzene solution, hydrogen chloride precipitated p-*nitrosobenzyl*-n-*butylaniline hydrochloride;* this, after being washed with benzene, dissolved in absolute alcohol, and reprecipitated by ether, was obtained in greenish-yellow, glistening plates, m. p. 138° with previous darkening (Found: Cl, 11·8. $C_{17}H_{20}ON_2,HCl$ requires Cl, 11·6%). It is readily hydrolysed by water.

The *base* was obtained by decomposing the hydrochloride with aqueous sodium carbonate; it crystallised from ether in green, glistening plates, m. p. 48—49°, which appeared steel-blue by reflected light (Found: N, 10·0. $C_{17}H_{20}ON_2$ requires N, 10·4%). When it was heated with concentrated hydrochloric acid, a pronounced odour of benzaldehyde was observed. On reduction with zinc dust and dilute sulphuric acid, it gave *benzyl*-n-*butyl*-p-*phenylenediamine*, which is described below.

4-p-*Sulphobenzeneazobenzyl*-n-*butylaniline*.—Solid diazosulphanilic acid was gradually added to a glacial acetic acid solution of benzyl-*n*-butylaniline. The mixture was shaken for 3 hours and diluted with water; the *azo*-compound then separated in well-defined, violet crystals (Found: S, 7·7. $C_{23}H_{25}O_3N_3S$ requires S, 7·6%). It forms a very soluble, orange *sodium* salt.

Benzyl-n-*butyl*-p-*phenylenediamine*.—Reduction of the preceding azo-compound (20 g.) by ammonium sulphide solution proceeded in the cold and was complete at the end of 24 hours. The precipitated oil was dissolved in ether, the solution washed with an aqueous suspension of lead carbonate to remove traces of ammonium sulphide, and the ether distilled off; *benzyl*-n-*butyl*-p-*phenylenediamine* was then obtained at 220—224°/12 mm. as a pale yellow oil (yield, 75%) (Found: N, 10·6. $C_{17}H_{22}N_2$ requires N, 11·0%), which slowly became red in the air.

The *sulphate* was obtained as a white solid from sulphuric acid and the amine in ethereal solution [Found: S, 5·6. $(C_{17}H_{22}N_2)_2,H_2SO_4$ requires S, 5·3%]. It is very soluble in alcohol and water. The *hydrochloride* was similarly prepared and obtained as a very hygroscopic, viscous precipitate. The *benzoyl* compound, prepared by the Schotten–Baumann reaction, was obtained in colourless needles, m. p. 131° (Found: N, 8·1. $C_{24}H_{26}ON_2$ requires N, 7·8%).

p-*Benzyl*-n-*butylaminobenzeneazo*-β-*naphthol*.—The green solution obtained by diazotising benzyl-*n*-butyl-*p*-phenylenediamine (prepared in either of the two ways mentioned above) in hydrochloric acid solution was freed from nitrous acid by means of carbamide and added to an alkaline solution of β-naphthol. The brown precipitate thus produced crystallised from alcohol in stout, dark red prisms with a greenish lustre; m. p. 133—134° (Found by the micro-method: N, 10·3. $C_{27}H_{27}ON_3$ requires N, 10·3%). With concentrated sulphuric acid, it developed a magenta colour, which changed to yellowish-orange on dilution.

The authors wish to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this work.

UNIVERSITY COLLEGE, CORK. [*Received, April 7th*, 1927.]

NOTES

The Estimation of Potassium in Presence of Iodide. By FRANK SWAIN HAWKINS and JAMES RIDDICK PARTINGTON.

THE estimation of potassium in presence of iodides is not easy. The cobaltinitrite method gives too high results. The chloroplatinate method cannot be used unless the iodide is first removed. When this is effected by cupric sulphate and sulphur dioxide, followed by precipitation of excess copper with sodium hydroxide, the results are low. Removal of iodide by silver nitrate, followed by hydrochloric acid to remove excess of silver, gives high results (102·3—105·4%). Reduction of the chloroplatinate obtained by any method to platinum by means of magnesium is unsatisfactory, since no specimen of magnesium used was completely soluble in hydrochloric acid. There is also the difficulty of the uncertain composition of the chloroplatinate precipitate (see Treadwell, "Quantitative Analyse," 1919, 39 ff.; the method given in the English translation is unsatisfactory). A modification of the perchlorate method was finally adopted. When an alkali iodide is evaporated to dryness with perchloric acid a sufficient number of times, the whole of the iodine can be expelled, but there is loss probably due to the fumes carrying over solid particles mechanically. Evaporation to the fuming point is insufficient. The following method gave good results. A saturated solution of potassium perchlorate in 96% alcohol is cooled to 0° and filtered. A saturated solution of sodium perchlorate is similarly prepared. The alkali iodides are dissolved in the alcohol saturated with potassium perchlorate, sufficient of the sodium perchlorate solution is added to precipitate all the potassium, and the solution is boiled, cooled to 0°, and filtered through a Gooch crucible. The precipitate is washed with the alcoholic potassium perchlorate at 0°, dried at 360°, and weighed. This gave results of the order of 99·95% with pure potassium iodide, the only error being due to a tendency of the precipitate to adhere to glass. By this method the sources of error described by Smith and Ross (*J. Amer. Chem. Soc.*, 1925, **47**, 774) are avoided. The method can be used for any potassium salts soluble in 96% alcohol.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON. [*Received, May* 11th, 1927.]

o-*Nitrobenzylphenyldimethylammonium Chloride.* By HLA BAW.

THE *m*- and *p*-nitro-isomerides of this compound have already been described (Wedekind, *Annalen*, 1899, **307**, 287; Peacock, *J. Soc. Dyers and Col.*, 1926, 53). When *o*-nitrobenzyl chloride and dimethylaniline in equivalent quantities were mixed and kept for some months, they slowly combined to form the *quaternary compound*, which separated in large, rhomboid crystals. These were washed with ether and recrystallised from alcohol–ether. The substance had a faintly yellow colour and turned green superficially on keeping; m. p. 99·5° (Found: Cl, 11·8, 11·6. $C_{15}H_{17}O_2N_2Cl$ requires Cl, 12·1%).—UNIVERSITY COLLEGE, RANGOON, BURMA. [*Received, April 25th*, 1927.]

A Spectrographic Method for the Determination of Dissociation Constants. By R. A. MORTON and A. H. TIPPING.

IT has been shown that the visible colour of solutions of violuric acid is due entirely to the violurate ion (J., 1925, **127**, 2514). Control determinations of p_H values with the quinhydrone electrode have enabled us to arrive at the value $e = 60$ for the extinction coefficient of a gram-ion of the acid radical. Hence it follows that, with a known initial concentration of violuric acid, the equation

$$K = [H^+][Vi^-]/[HVi_{undiss.}] = [Vi^-]^2/([HVi_{total}] - [Vi^-]) \quad . \quad . \quad (1)$$

allows of the evaluation of the dissociation constant from a spectroscopic determination of the concentration of the violurate ion.

For example, a solution of 0·00306*N*-violuric acid in a 30 cm. cell has e max. 0·42 at the position of maximum absorption. From the relation $\log I_0/I = ecd$, $0{\cdot}42 = 60 \times x \times 30$; *i.e.*, x, the concentration of violurate ion, = 0·000233. Hence $K = (0{\cdot}000233)^2/(0{\cdot}00306-0{\cdot}000233)$ or $1{\cdot}92 \times 10^{-5}$.

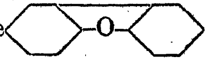
A simple extension of this work enables us to determine the dissociation constants of weak acids which obey the dilution law: If for a mixture of violuric acid of concentration [HVi] with another acid of concentration [HA] the value of $\log I_0/I$ at the position of maximum absorption is found, it is clear from the relation log $I_0/I = ecd$ that the concentration of the violurate ion can be obtained. [HVi] and [Vi^-] are thus known, so that the concentration [$HVi_{undiss.}$] of the undissociated acid follows. From equation (1) [H^+] can be determined, since K is known. The mixture is electrically neutral, so that $[H^+] = [Vi^-] + [A^-] + [OH^-]$. In acid solutions [$OH^-$] is negligible, so that $[H^+] = [Vi^-] + [A^-]$. In this equation [A^-] is the only unknown quantity and can therefore be evaluated. The concentration [HA] originally used is known, so that $[HA_{undiss.}] = [HA] - [A^-]$. Hence $K_{HA} = [H^+][A^-]/[HA_{undiss.}]$.

The following results were obtained :

Acid.	*K.*	Standard values.
Acetic	1·5—1·8 × 10^{-5} at 18°	1·82 × 10^{-5} at 18°
,, ...	1·5—1·9 × 10^{-5} at 19°	,,
,, ...	1·7—2·0 × 10^{-5} at 20°	,,
Chloroacetic	1·4—1·7 × 10^{-3} at 18·5°	1·55 × 10^{-3} at 25°
Glycollic	1·3—1·6 × 10^{-4} at 19°	1·5 × 10^{-4} at 25°
Salicylic	1·0—1·2 × 10^{-3} at 19°	1·04 × 10^{-3} at 20°

The method can also be extended to the determination of the distribution of a base between violuric acid and another weak acid. This has been verified for mixtures of acetic and violuric acids.—THE UNIVERSITY, LIVERPOOL. [*Received, December 1st*, 1926.]

*Reduction Products of Some Nitrodi-*p*-tolyl Ethers.* By JOSEPH REILLY and HERBERT S. BOYD BARRETT.

AS an extension of previous work (this vol., p. 67) the preparation of 3-nitro-, 3- and 2-amino-di-*p*-tolyl ethers, the partial reduction of the 2 : 6-dinitro-compound, and the nitration of 2-nitrodi-*p*-tolyl ether are now described. The 2-diazonium chloride derivative, $C_6H_4Me{\cdot}O{\cdot}C_6H_3Me{\cdot}N_2Cl$, on decomposition gave a tar-like product from which di-*p*-tolylene ether, MeMe, and chlorodi-*p*-tolyl ether were isolated in small amounts.

3-*Nitrodi-*p*-tolyl ether* was prepared by heating potassium *p*-tolyloxide (21 g.) and 4-bromo-2-nitrotoluene (27 g.) with *p*-cresol (40 g.) (solvent) and copper bronze (0·2 g.) at 230—240° for 3 hours. On fractionation of the dried ethereal extract under diminished pressure, the 3-*nitro*-compound was obtained as a pale yellow oil, b. p. 206°/11 mm. (Found : N, 5·8. $C_{14}H_{13}O_3N$ requires N, 5·7%). It is freely soluble in benzene and ether, much less so in cold alcohol, and insoluble in water. Reduction with stannous chloride and hydrochloric acid gave the corresponding amine. The *hydrochloride* of this was obtained in colourless needles, m. p. 190—195° (Found: Cl, 14·2. $C_{14}H_{15}ON,HCl$ requires Cl, 14·2%). The *base* prepared from the hydrochloride separated from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 76° (Found: N, 6·5. $C_{14}H_{15}ON$ requires N, 6·6%). It is readily soluble in benzene, ether, and acetone, less so in light petroleum, and insoluble in water. The *benzoyl* compound separated from light petroleum in clusters of stout needles, m. p. 107° (Found: N, 4·2. $C_{21}H_{19}O_2N$ requires N, 4·4%). 3-*Aminodi*-p-*tolyl ether chloroaurate* is a bright yellow, crystalline solid (Found: Au, 35·1. $C_{14}H_{15}ON,HAuCl_4$ requires Au, 35·6%). The *azo*-β-*naphthol* compound separated from alcohol in red plates, m. p. 149° (Found: N, 7·8. $C_{24}H_{20}O_2N_2$ requires N, 7·6%).

2-Nitrodi-*p*-tolyl ether was similarly reduced. The 2-*amino*-derivative on fractionation distilled at 196—198°/13 mm. as a colourless oil, which did not solidify at − 15° (Found: N, 6·3. $C_{14}H_{15}ON$ requires N, 6·6%). The *hydrochloride*, colourless blades, m. p. 180—184°, and the *sulphate*, m. p. 160—162°, were prepared. The addition of the 2-diazonium chloride solution to boiling sulphuric acid (50%), followed by distillation in a current of steam, gave a colourless oil which quickly solidified. This solid was separated by fractional crystallisation into two substances of m. p.'s 70° and 165°. The latter substance was identified as a di-*p*-tolylene ether by the method of mixed melting point. The compound, m. p. 70°, appeared to be 2-chlorodi-*p*-tolyl ether.

Partial reduction of 2 : 6-dinitrodi-*p*-tolyl ether between 50° and 60° with stannous chloride gave the 6-*nitro*-2-*amino*-derivative. The *hydrochloride*, m. p. 206—210°, crystallised from ether–alcohol in colourless rosettes. The pure base, m. p. 120—122°, obtained from the hydrochloride, separated from light petroleum (b. p. 80—100°) in light yellow needles. On diazotisation in hydrochloric acid it gave an unstable product. The *azo*-β-*naphthol* compound was obtained as a dark brown, crystalline solid, m. p. 190—200° (Found: N, 10·4, $C_{24}H_{19}O_4N_3$ requires N, 10·2%).

Nitration of 2-nitrodi-*p*-tolyl ether with nitric acid (*d* 1·5) gave mainly 3 : 5-dinitro-*p*-cresol, together with 2 : 2′-dinitrodi-*p*-tolyl ether, m. p. 126°.—UNIVERSITY COLLEGE, CORK. [*Received, April* 11*th*, 1927.]